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A SURVEY OF AMERICAN CHEMISTRY

VOLUME I

JULY 1, 1925 TO JULY 1, 1926

Including
Reports from Scientific Committees,
Division of Chemistry and Chemical Technology,
National Research Council

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FOREWORD

In order that the chemists of America may be given a perspective of the advance made in their several fields of research and in order that the importance of certain prospective researches may be adequately emphasized by those most qualified to express opinion, the Division of Chemistry and Chemical Technology of the National Research Council has essayed to bring together in this volume a number of articles from well-known scientific authorities.

This presentation covers only the literature of that period embraced by the past fiscal year of the National Research Council. In several instances the articles comprise the annual reports of certain scientific committees of the Division of Chemistry and Chemical Technology. In general, the articles have been drawn up to cover the fundamental subjects of present day interest.

It is to be hoped that, as succeeding volumes appear, there may be added a number of articles dealing with scientific and industrial activities of a more diversified nature.

A roster of the Division of Chemistry and Chemical Technology for the period covered is introduced on the following page inasmuch as the activities of the Division are typified in this compilation.

The Executive Committee of the Division wishes, at this time, to acknowledge its appreciation of the services rendered by Dr. Clarence J. West, Chairman of the Committee on Publications and Publicity of the National Research Council, for his careful scrutiny of the manuscript. All abbreviations are made to accord with those adopted in publications of the American Chemical Society.

WILLIAM J. HALE.

December 15, 1926.

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Chapter I.

Aluminum.

FRANCIS C. FRARY,
Director of Research, Aluminum Company of America.

Production.

One of the larger items in the cost of producing a pound of aluminum is the manufacture of the two pounds of purified aluminum oxide required. T. R. Haglund[1] proposes a new method for this, by electrothermally melting bauxite with pyrites and carbon, to produce a purified slag of alumina and aluminum sulfide. The small amounts of oxides of iron, silicon and titanium remaining are largely associated with the aluminum sulfide matrix, and by dissolving this in acids or decomposing it with steam and washing, purified crystals of aluminum oxide are produced.

Minor improvements in connection with the Hoopes process of producing aluminum by electrolytic refining have been disclosed during the year.[2]

Railsback[3] proposes to replace the cryolite, used in the electrolytic reduction of alumina, with a double fluoride of aluminum and a metal whose oxide is not reducible by aluminum, such as Li, Be, Mg, Ca, Sr and Ba, and to add sulfides, chlorides, etc., to the bath so as to reduce the decomposition voltage and save power. His suggestions can hardly be considered practical.

Properties.

Anderson[4] finds by X ray methods that duralumin has a face-centered cubic lattice substantially identical with the aluminum lattice. Addition to aluminum of copper up to 4% has no effect on the aluminum lattice, but about 6% copper contracts it slightly.

[1] Ind. Eng. Chem., 18: 67; 1926. U. S. P. 1,569,483; Jan. 12, 1926.
[2] Tilson, U. S. P. 1,572,253; F. C. Frary, U. S. P. 1,572,475; Feb. 9, 1926.
[3] U. S. P. 1,566,694; Dec. 22, 1925.
[4] J. Franklin Inst., 201: 465; 1926.

Diffraction patterns of duralumin sheet after various treatments are shown and discussed. The same author [5] recommends the use of the X-ray for the detection of porosity and other flaws in aluminum castings.

Sachs and Schiebold [6] have studied the process of annealing pure aluminum wire, using the X-ray patterns. These show that recrystallization begins at about 200° C., but does not become general until the annealing temperature of 250° C. is reached, although annealing at as low a temperature as 100° C. begins to produce a softening, as shown by decrease in tensile strength.

Alloys.

Since copper is the most important alloying element employed in high-strength aluminum alloys, the equilibrium in the system aluminum-copper is of the greatest interest. Dix and Richardson [7] have re-investigated this, using aluminum of a much higher purity (99.917%) than previous investigators, and with improved technique. The most important change is in the curve of solid solubility of copper in aluminum, which is of basic importance in the heat-treatment of aluminum-copper alloys. It is found that there is a very rapid decrease in solubility with falling temperature, from a little over 5.5% at 548° C. to about 2% at 430° C., the curve here being practically a straight line. The rate of decrease slows up markedly between 430° and 300° C., and is very slight below 300° C. At room temperature the solubility is certainly less than 0.5%. The absence of appreciable quantities of other metals in the specimens made the determination of the curve by metallographic examination much more accurate than it could be with the grade of metal previously available. Photomicrographs of typical structures are shown, together with some showing for the first time the reprecipitation of copper during artificial aging of heat-treated aluminum-copper alloys.

In another investigation with this high purity aluminum, Dix [8] has shown that the eutectic in the system aluminum-iron, in the absence of silicon and copper, lies at about 1.7% iron and melts at about 655° C. A series of twenty photomicrographs illustrate characteristic forms of the pure constituent, $FeAl_3$, produced under

[5] Iron Trade Rev., **77**: 374; 1925.
[6] Z. Metallkunde, **17**: 400; 1925.
[7] Iron Age, **117**: 554; 1925.
[8] Proc. Am. Soc. Testing Materials, **25** II: 120; 1925.

different conditions. These studies of the pure binary systems are preliminary to a study of the more complicated ternary and quaternary ones.

The "modification" and properties of sand-cast aluminum-silicon alloys have been discussed by Archer and Kempf [9] on the basis of an extensive experimental study of the theory and practice of casting and "modifying" these alloys. Modification is brought about by the introduction of a minute amount of metallic sodium, and consists in shifting the apparent eutectic point of the alloys from 11-12% to 14% silicon, and causing the precipitation of the silicon in extremely finely divided form. This improves both strength and elongation. The maximum improvement is only obtained with a very definite but small sodium content, probably only a small fraction of the 0.01% to 0.10% of sodium added to the alloy. With perfect modification, the best combination of physical properties is obtained at the modified eutectic (14% silicon), but for practical use a somewhat lower silicon content (about 12.75%) is preferable, on account of the difficulty of always obtaining perfect modification. The addition of iron above 0.35% to the modified alloys decreases their elongation: from 0.35% to 0.75% iron there is a slight increase in tensile strength, while more than 0.75% iron decreases the tensile strength.

The modification of silicon alloys can also be produced by chill-casting [10] and the addition of certain other metals improves the properties of silicon alloys, especially chill-castings.[11] Hobbs [12] has discovered the rather surprising fact that if sand-cast articles of aluminum-silicon alloys, preferably "modified," are removed from the molds very promptly and cooled quickly, as by quenching them in water, the tensile strength, yield point and hardness are all decidedly raised. This is probably due partly to the retaining of a somewhat larger quantity of silicon in solid solution, and partly to preventing the growth of the precipitated silicon particles.

The basis of the heat-treatment of castings of aluminum-copper alloys, which has grown to considerable industrial importance during the past three or four years, is disclosed by

[9] Iron Age, 117: 554; 1925.
[10] Archer and Edwards, U. S. P. 1,572,459; Feb. 9, 1926.
[11] Pacz, U. S. P. 1,572,502-3; Feb. 9, 1926. Johnston, Archer and Jeffries, U. S. P. 1,572,489-90; Feb. 9, 1926. Johnston, U. S. P. 1,572,357; Feb. 9, 1926. Crosby, U. S. P. 1,572,382; Feb. 9, 1926.
[12] U. S. P. 1,570,893; Jan. 26, 1926.

Jeffries and Archer [13] to be a proper control of the alloy composition, especially the percentage of iron, and a very long time of heat-treatment (up to 48 hours). They have likewise found [14] that a corresponding heat-treatment of castings of aluminum-silicon alloys changes the shape and sometimes the size of the silicon particles and very markedly increases the ductility of the castings.

Daniels [15] has studied the effect of heat treatment on aluminum piston alloys of the ordinary type (Al-Cu-Fe-Mg) and of the Y alloy type (Al-Cu-Ni-Mg), and prefers the latter, in the heat-treated state, for service where the pistons are likely to become very hot, as in aircraft motors.

Aluminum does not alloy with more than traces of sodium and potassium, but with lithium it forms a series of alloys which, according to Assmann,[16] are stable up to about 10% lithium, but oxidize rapidly above this point. This author has studied the equilibrium in the aluminum-lithium system up to 12% lithium, and finds a eutectic at 7.8% lithium. Aluminum-lithium alloys are capable of improvement by heat-treatment: the solid solubility of lithium in aluminum is about 3.5% at the freezing point of the eutectic (598° C.) and 2.2% at room temperature. The hardening effect of lithium is somewhat greater than that of magnesium. Like magnesium, it makes the heat-treated aluminum alloys containing copper "age" at room temperature, but if there is as much as 1% of lithium present this facilitation of the precipitation and coalescence of the dissolved copper is so powerful that the alloys become over-aged and softened when exposed to temperatures as low as 100° C.

The effect of artificial aging on other aluminum alloys is discussed by Gayler [17] and Meissner.[18]

Fuller and Basch [19] have patented a casting alloy containing 3-8% zinc and 0.25-1.5% magnesium, which is said to be capable of improvement by heat-treatment.

Daniels [20] has studied the mechanical properties and metallography of aluminum-manganese alloys, and confirms the previously known resistance of these alloys to corrosion, and the fact

[13] U. S. P. 1,572,487; Feb. 9, 1926.
[14] U. S. P. 1,572,488; Feb. 9, 1926.
[15] Trans. Am. Inst. Mining Met. Eng., 73: 479; 1925.
[16] Z. Metallkunde, 18: 51; 1926.
[17] Metal Ind. (London), 27: 30; 1925.
[18] Metal Ind. (London), 27: 483; 1925. 28: 363; 1926.
[19] U. S. P. 1,578,979; Mar. 30, 1926.
[20] Ind. Eng. Chem., 18: 125; 1926.

that not over 2% of manganese can be used advantageously in casting alloys. Photomicrographs illustrate typical microstructures.

Flick [21] has studied various etching reagents for use in bringing out the crystalline structure of cast and wrought aluminum, and finds that the best results are obtained with a mixture of hydrofluoric and hydrochloric acids.

[21] Trans. Am. Inst. Mining Met. Eng., 71: 816; 1925.

Chapter II.

Chromium.

Colin G. Fink,

Professor of Electro-Chemistry, Department of Chemical Engineering, Columbia University.

A few years ago it was pointed out that modern civilization was entering upon a new metal age, namely, the "chromium age." Since then developments have been in leaps and bounds. Electrically heated ovens for enamelling and baking, using chrome-nickel resistors, are universally employed: stainless steel, in which the presence of the 13% chromium spells "stainless," is familiar to all housewives: with the persistent higher wage scale for machinists and all metal workers high speed chrome-tungsten steels have largely replaced the old carbon tool steels: ferro-chromes containing 60% and more of chromium are readily made in the electric furnace today, with carbon content down to 1% and less, a feat impossible of attainment in our old fuel fired furnaces; finally, the introduction of chromium plating has revolutionized the plating industry throughout the world. The plate can be made harder than the hardest file, more resistant to corrosion than any other plate, except gold, resistant to high temperatures and most acids.

The natural source of chromium is the mineral chromite, $FeCrO_4$, contained in the earth's crust in greater abundance than the combined copper minerals. Commercial deposits of chromite have been located in different parts of every continent of the globe. Valuable mines are in California and in Maryland and during the last year of the war the United States was the foremost producer of chromite. Today the Rhodesian mines supply over 50% of the world's requirements. During the past ten years the world's production of chromite has more than tripled, a record

not even approached by metals such as aluminum, copper, silver, nickel, iron, tin, lead or zinc.

During the period July 1, 1925, to July 1, 1926, the following are among the more important of the numerous researches and reports published by American investigators.

Physical and Chemical Studies.

R. A. Patterson [1] of the Rensselaer Polytechnic Institute has carefully measured the crystal structure of chromium metal, analyzing 99.8% Cr, using the standard X-ray diffraction apparatus developed by Hull and Davey. The diffraction patterns confirm the body-centered cubic structure previously found by Hull with $a_0 = 2.872$ Å units. The computed density is 7.23 grams per cubic centimeter as compared with 6.92, the value determined by Moissan by direct weighing and 7.1, the value recorded in the new International Critical Tables.

Coagulation experiments, made by S. Ghosh and N. R. Dhar,[2] with negatively charged chromium hydroxide [$Cr(OH)_3$] sol showed that the behavior of the sol is normal. In other words, practically an additive relationship of the precipitation value was obtained when the sol was precipitated by mixtures of electrolytes of widely varying precipitating powers. The greater the concentration of sol the greater the amount of electrolyte necessary for its coagulation. When the sol was coagulated by a mixture of electrolytes, the coagulation power of the mixture was an additive function of the coagulating powers of the individual electrolytes.

K. H. Gustavson [3] investigated the effect of NaCl additions to solutions of chromic chloride, in particular the effect on the hydrogen ion concentration and stability towards alkali. The first small additions of NaCl caused a decrease in the H ion concentration. Further additions caused a steady increase in the H ion concentration. The addition of NaCl brings about a stabilization of chlorine in the coordinate sphere. The data are in accord with the hydration hypothesis in combination with the concept of the chromium compounds, on the basis of the coordination theory. The investigation has a direct bearing on the chrome tanning industry.

[1] Phys. Rev., 26: 56; 1925.
[2] J. Phys. Chem., 29: 435; 1925.
[3] Ind. Eng. Chem., 17: 945; 1925.

Another investigation by Gustavson [4] deals with the fixation of constituents of chrome liquors by hide substance from highly concentrated chrome solutions. By plotting the amount of chromium fixed by hide substance under uniform conditions against the concentration of basic chrome liquor, Gustavson obtained a curve having a maximum at 17 g/l of Cr_2O_3, then a minimum at 120 g/l, a second maximum at 140, a second minimum at 180 and a third maximum at 193 g/l. The chromium complexes in the concentrated liquor are not all of the same charge, some being positively charged and some negatively. This complicates the primary reaction between Cr ions and collagen. However, the results can be explained only on the basis of a chemical conception of chrome tanning. The addition of Na_2SO_4 to chrome liquors causes some of the chromium ions to enter negative complexes and to give a fuller leather in tanning which is characteristic of the tannage with these complexes.[5]

The Grasselli Dyestuff Corporation [6] has patented the production of basic chromic salts. Solutions of chromic salts are acidulated with sulfuric acid in the proportion of 140 or less parts of SO_3 to 152 parts of Cr_2O_3 and the solutions atomized into a stream of hot gas.

Metallurgical Studies.

The metallurgical investigations on chromium far outnumber the investigations on the physics and chemistry of chromium. Furthermore, numerous patents on chrome steels and other chrome alloys have been issued during the fiscal year 1925 to 1926.

Stainless Steels. W. G. Whitman and E. L. Chappell [7] reported on the corrosion of steels in the atmosphere and showed that with chromium steels, the corrosion decreased rapidly as the chromium content was increased from 8% up to 16% Cr. P. A. E. Armstrong and R. P. de Vries have patented stainless steels suitable for cutlery. In one patent [8] they specify the following composition: C 0.05% up to 0.60%, Cr 5% to 9%, Si over 1%; Ni and Si together sufficient to make the combined percentage of nickel, silicon and chromium equal to 12% to 15%, the remainder being mainly iron. In order to render stainless steels and stain-

[4] Ind. Eng. Chem., 17: 823; 1925.
[5] J. Am. Leather Chem. Assoc., 20: 382; 1925. *See also* Rogers, J. Chem. Education, 2: 363; 1925. Burton, J. Soc. Leather Trades Chem., 9: 383; 1925.
[6] Roessner and Runne, U. S. P. 1,592,961; July 20, 1926.
[7] Ind. Eng. Chem., 18: 533; 1926.
[8] U. S. P. 1,555,395; Sept. 29, 1925.

less irons more resistant to food acids Armstrong [9] recommends heating the alloys considerably above their upper transformation points and then rapidly cooling. O. M. Otte [10] finds that these alloys are rendered more resistant to corrosion by giving them a preliminary treatment in a solution of nitric acid.

Chrome-Tungsten Steels. U. P. Gill and M. A. Frost [11] critically studied the analyses of seventy-five tool steels. They find that non-deformable oil-hardening tool steels are improved by the addition of 0.5% of chromium and tungsten. Uniform hardening is assisted by the addition of 0.5% chromium. Cold drawing dies are generally made of steel containing 11% to 15% Cr and 1.5% to 2.5% C. According to John A. Mathews [12] austenite is always present with martensite in hardened steels. Possibly the real function of Cr, Mn, Ni, V, and Mo in steel is to promote the retention of austenite. T. Spooner [13] of the Westinghouse Company reviews the properties and testing of magnetic alloys. The alloy containing 9% to 14% Cr, 1% C, 1% to 18% Co, but no tungsten, and the balance iron, is self hardening and possesses magnetic properties but little inferior and at a lower cost than the best Japanese or tungsten steels.

Ferro-Chromes. E. C. Bain of the Union Carbide Research Laboratory examined metallographically two series of alloys of iron with chromium up to 35% Cr and containing 0.1% to 0.26% C and 0.26% to 0.50% C respectively. In the preparation of the alloys Bain used Armco iron and low carbon ferro-chrome. The alloys were quenched from seven different temperatures between 900° and 1450° C. He found that the austenite in the low carbon alloys required a high temperature for decomposition but was not resistant to cold work. The American Society for Testing Materials recommended (1925) for the determination of chromium in ferro-chrome: fusing with sodium peroxide, extracting with water, reducing the Na_2CrO_4 with ferrous iron and titrating the excess of Fe^{++} with standard $KMnO_4$ solution.

Nickel-Chromes and Cobalt-Chromes. P. H. Brace [14] of the Westinghouse Company finds that the addition of tantalum to nickel-chrome alloys renders them very resistant to acids and oxidation. The composition may be varied within wide limits:

[9] U. S. P. 1,554,615; Sept. 22, 1925.
[10] U. S. P. 1,549,022; Aug. 11, 1926.
[11] Trans. Am. Soc. Steel Treating, 9: 75; 1926.
[12] Engineering, 120: 368; 1925.
[13] Elec. J., 22: 394; 1925.
[14] U. S. P. 1,588,518; June 15, 1926.

5% to 30% Cr added to nickel-tantalum alloys containing from 25% to 99% Ta. P. Girin[15] investigated the malleability of nickel-chromes and found that if the composition is kept within the following limits the alloy can be rolled and drawn into fine wire: 20% to 40% Ni, 10% to 15% Cr, 1% to 5% Mn, 0.2% to 1.0% C, balance Fe. R. L. Spitzley and A. M. Thompson[16] recommend the addition of small percentages of silicon, tungsten and copper to the nickel-chromes. One of the preferred compositions has 56% Ni, 8% Cr, 7% Mn, 26% Fe, 2% Si and 1% W. Of the various new cobalt-chromes, or alloys of the stellite type, that of B. M. Huff is well suited for cutting tools: 40% to 50% Co, 25% to 35% Cr, 5% to 15% W, 1% to 1.5% Mn, 1% to 5% Si and 0% to 5% Fe.

Alloys of Aluminum and Chromium. F. T. Sisco and M. R. Whitmore[17] of the Government Air Service, interested in improving the mechanical properties of aluminum, prepared a series of alloys of aluminum and chromium. Chromium alloys easily with aluminum but it increases the shrinkage of aluminum to a very marked extent. The alloy is apparently $AlCr_3$. The tensile strength is higher than that of pure aluminum but the alloys produced were all very brittle, thus eliminating immediate commercial application.

Chromium Metal. The old process of producing the metal by the Goldschmidt thermit reaction has been almost entirely displaced by the electric furnace process. On the other hand, the Metal Research Corporation[18] smelts a mixture of oxide of chromium, soda and coke in a blast furnace in such a way that the metallic sodium first liberated reduces the chromium oxide to metallic chromium. The electrodeposition of metallic chromium and chromium alloys on steel, brass, copper and other metals is now being carried out on a large commercial scale. The researches of Fink, C. H. Eldridge, Hugh McLease and others have established the chromic acid bath on an easily reproducible basis. The hydrogen cathode film must be maintained at a well defined thickness and consistency. Pure chromium metal is malleable and ductile.

[15] U. S. P. 1,542,233; June 16, 1925.
[16] U. S. P. 1,587,992; 1,587,993; 1,587,994; June 8, 1926.
[17] Ind. Eng. Chem., 17: 956; 1925.
[18] Strong, Parsons and Peacock, U. S. P. 1,581,698; Apr. 20, 1926.

Chapter III.

Copper.

WILLIAM H. BASSETT,

Technical Superintendent & Metallurgist, The American Brass Company.

The metallurgy of copper is a broad subject and in reviewing the progress made during the past year it is necessary to limit this survey to the refining and technology of copper and to progress in the field of copper alloys.

Refining of Copper.

The marked advances in copper refining during the past year may be summarized as follows:

1. The control of the resistance of the electrolyte in electrolytic refining resulting in marked saving of power in the tank house. A few years ago, 150 grams per liter was the usual sulfuric acid strength of the electrolyte. The present acidity will range from 200 to 220 grams per liter, requiring considerably less consumption of power per unit of copper deposited.

2. The use of pulverized coal or fuel oil superseding the semi-producer fire box for refining furnaces, resulting not only in more economical operation, but also better copper. The features and advantages of a pulverized coal installation at Anaconda have been described by Bardwell and Miller.[1]

3. The use of the microscope in controlling the work of the refining furnace. This is scientifically a marked advance in the art of copper refining. The "rabbling" to set copper and the "poling" to "tough pitch" copper are controlled in at least three of the large refineries by determining the oxygen content of the copper by means of the microscope. A method of analysis based on microstructure was described in 1913 by Bardwell,[2] who

[1] Trans. Am. Inst. Mining Met. Eng., Preprint; 1925.
[2] Trans. Am. Inst. Mining Met. Eng., 46: 742; 1913.

developed a method along the lines suggested by the work of Hofman, Green and Yerxa.[3]

4. The recovery of by-product metals other than silver and gold is receiving careful attention. Selenium is used extensively in the manufacture of glass, and the refineries are able to dispose of most of their production. An appreciable amount of nickel salts used in electroplating is furnished by the copper refineries. All refineries are now recovering small amounts of platinum and palladium.

5. The macrostructure as well as the microstructure of wire bars and other copper castings is the subject of considerable recent study both in Europe and America. The effect of structure on working properties is having attention.

Technology of Copper.

At the meeting of the American Institute of Mining and Metallurgical Engineers in New York, in February, 1926, a symposium on the properties of copper was held and several papers were presented covering different phases in the technology of copper. For the purpose of showing the general trend of development, it will perhaps be sufficient to list these papers by title:

Bassett, W. H., and Bedworth, H. A. (The American Brass Co.): Estimation of oxygen and sulfur in refined copper. Trans. Am. Inst. Mining Met. Eng. 73: 784; 1925.

Bassett, W. H., and Bradley, J. C. (The American Brass Co.): Exudations on copper castings. Trans. Am. Inst. Mining Met. Eng. 73: 700; 1925.

Bassett, W. H., and Bradley, J. C.: Action of reducing gases on heated copper. Trans. Am. Inst. Mining Met. Eng. 73: 755; 1925.

Fuller, T. S. (General Electric Co.): Embrittlement of copper by hot reducing gases. Trans. Am. Inst. Mining Met. Eng. 73: 744; 1925.

Hoyt, S. L., and Schermerhorn, T. R. (General Electric Co.): Hardness of copper and Meyer's analysis. Trans. Am. Inst. Mining Met. Eng. 73: 657; 1925.

Leiter, Susan B. (General Electric Co.): Annealing of commercial copper to prevent embrittlement. Trans. Am. Inst. Mining Met. Eng. 73: 776; 1925.

Pilling, N. B., and Halliwell, G. B. (Westinghouse Electric and Manufacturing Co.): Effect of lead and tin with oxygen on the conductivity and ductility of copper. Trans. Am. Inst. Mining Met. Eng. 73: 679; 1925.

Following the presentation of these papers there was considerable discussion of the relative merits of oxygen-free and ordinary refinery copper. There is an increasing demand for oxygen-free copper for certain engineering and electrical uses. Such

[3] Trans. Am. Inst. Mining Met. Eng., 34: 671; 1904.

material is especially suitable for use where reducing gases at high temperatures are encountered, or where severe mechanical manipulation is concerned, or on account of its better resistance to certain corrosive conditions. Boron compounds have been successfully used for producing a special type of deoxidized copper having high electrical conductivity. Economy of production is in favor of "tough pitch" copper and it is therefore generally used for alloying purposes, for electrical use where high electrical conductivity is essential, and for most architectural and engineering needs.

Copper Alloys.

Architecture and engineering are learning the value of copper and copper alloys. The demand for these metals is continually increasing. There has been considerable advance in the production of alloys with high tensile strength and at the same time relatively high electrical conductivity for use in electrical conductors. Notably, alloys of copper with small amounts of such metals as cadmium, tin, aluminum and silicon are used for this purpose.

Silicon is coming into use to a considerable extent as a hardening and strengthening agent for copper, replacing tin for this purpose and also increasing the resistance to corrosion.

In the field of welding, there has developed a large use for copper alloys for welding iron and steel. The alloys used are Tobin bronze, Manganese bronze, Phosphor bronze and Silicon bronze.

The study of corrosion problems is assuming a position of primary importance to the industries. Rapid advance is being made not only in the collection of data, but also in the development of alloys to meet and withstand corrosive conditions. No "universal" alloy is known to meet successfully the wide variety of industrial requirements, and the development is in the direction of a number of alloys, each suited to a particular type of service. A number of corrosion-resistant copper alloys have been proposed during the past few years and some of these are being used extensively in the chemical and allied industries. From the more recent researches it does not seem likely that any alloy will be found to satisfactorily resist all corroding substances. Special alloys will have to be devised for particular service conditions.

RESEARCH PROBLEMS.

Some important research problems connected with copper and its alloys are the following:

Considerable is known concerning the effect of impurities and small amounts of alloying metals on the physical and electrical properties of copper but there is still much to be learned in this direction. A careful study of the effect of small quantities of almost any metal or metalloid soluble in copper would give valuable data. Considerable work in this direction is now being carried on.

The rapidly increasing use of copper alloys as welding material makes the study of welding problems important. A research into the efficiency of various copper alloys and various fluxes for welding iron and steel would be likely to result in important information. Another interesting field for research would be the nature of welds, that is, what makes the weld hold. Is an alloy formed by the welding material with the steel or iron parts which are being welded together, and if so, what are the natures and characteristics of these alloys?

The study of corrosion is being seriously and vigorously undertaken not only by the industries, but by schools, universities and various technical societies. There is more to be known regarding the mechanism and fundamental principles of corrosion, and their application to practice. There are at the present time no generally accepted laboratory methods for testing the corrodibility of alloys and much work is being done toward the development of suitable methods. The American Society for Testing Materials is actively carrying out an extensive investigation of various types of test, which study will in time yield valuable results, but the problem is so broad and so diversified that constructive research in this field will be welcomed. On the practical side, data are being collected covering the performance of corrosion-resistant alloys by laboratory and service tests, and additional data of this sort would be of general value to industry.

Chapter IV.

Iron and Steel.

HERBERT M. BOYLSTON,

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Developments in the iron and steel industry are many and varied. The subject of the beneficiation of lean iron ores is becoming more important as the reserves of high grade ore in the Lake Superior region begin to show depletion and as the operators begin to realize that within ten to fifteen years it will be necessary to utilize the leaner ores. Already more than 25% of all ore shipped from this region is being washed or concentrated. Experiments are being made looking toward the improvement of blast furnace practice and design.

The Open Hearth Committee of the American Institute of Mining and Metallurgical Engineers has held several conferences leading to the more wide-spread knowledge of open hearth melting practice and design and considerable progress has been made in commercial applications of improvements in design of open hearth furnaces and auxiliary apparatus. A commercial plant for the manufacture of electrolytic iron tubes and sheets has been established on a rather large scale.

A new recording pyrometer having interchangeable parts and two new binocular microscopes for the study of sands, ores and the structures and fractures of metals under low magnifications have appeared on the market. Extensive researches have been conducted on the physical properties of steel at room temperatures as well as at high temperatures. Many important developments in the metallography and heat treatment of iron and steel have been reported.

Iron Ore.

E. W. Davis, at a meeting of the Associated Technical Societies of Cleveland, May, 1926, spoke on "Progress in the Beneficiation

of Minnesota Iron Ores." [1] He pointed out that "in ten years or possibly less time, many of the operators will be running short of merchantable ore." He called attention to the fact that the removal of coarse silica from low grade ores is the real problem, while selective abrasion and magnetic concentration have been tried. He also spoke of progress made with a method for the direct reduction of iron ores.

M. C. Lake [2] states that the Lake Superior district furnishes from 80% to 85% of all the iron ore annually consumed in the United States, at the rate of 50,000,000 to 60,000,000 tons per annum, that reserves of only 1,500,000,000 tons are known and that beyond that quantity low grade ores must be beneficiated. He also stated that in 1914, 0.1% of the ore shipped from Minnesota was beneficiated; that in 1924, 24.4%, and that in 1925 about 35% was subjected to this treatment.

In discussing this paper, W. G. Swart [3] checks Lake's figures as to iron ore reserves and calls attention to increased mining cost, competition of foreign ore, changes in furnace location and practice and unequal ownership which will affect future production.

W. O. Hotchkiss [4] agrees with Lake, Swart and Davis in their estimates.

C. Zapffe [5] points out that there are two principal sources of manganiferous iron ores. He describes previous production and states that ample reserves are available. C. P. McCormack [6] shows that when metallurgical methods are adjusted so that run-of-mine ore can be used, the manganiferous iron ore of the Cuyuna district might easily be a principal source of manganese for the iron and steel industry in the United States.

Sponge Iron.

E. P. Barrett and B. M. Larsen at the Northwest Experiment Station of the U. S. Bureau of Mines are developing a commercial method for the production of sponge iron direct from iron ore with the object of furnishing a material for precipitating metals such as copper, silver or lead from solutions or as an inexpensive metal for conversion into iron or steel by melting.

[1] Mining and Met., 7: 280; 1926.
[2] Mining and Met., 7: 325; 1926.
[3] Mining and Met., 7: 334; 1926.
[4] Mining and Met., 7: 339; 1926.
[5] Mining and Met., 6: 573; 1925.
[6] Mining and Met., 6: 247; 1925.

Ferro-Alloys.

W. J. Priestley [7] has described metals and ferro-alloys used in the manufacture of steels.

Specifications covering the leading ferro-alloys are being considered by a Committee on Ferro-Alloys of the American Society for Testing Materials.

The Foundry.

The problem of obtaining and testing the proper kinds of sand for foundry molds has been one of the chief subjects of discussion before the American Foundrymen's Association.

A method of recording the temperature of molten cast iron as it issues from the cupola has been successfully worked out by H. W. Dietert and Wm. Myler.

Electrolytic Iron.

The production of electrolytic iron tubes on a fairly large commercial scale was begun at Niagara Falls by the Niagara Electrolytic Iron Company.[8] An inexpensive anode of cast iron, cast directly at the blast furnace, is used and the highly ductile product is said to contain frequently not over 0.05% of the usual five impurities: carbon, manganese, phosphorus, sulfur and silicon. Material will be available for cartridges, oil cans, vacuum bottles, bottles for ammonia, metallic hose and for general deep drawing for a wide variety of purposes.

The Open Hearth Process.

At one of the Alabama plants, four new 125 ton stationary open hearth furnaces were put into operation. These are equipped to burn tar, by-product gas or oil and have a unique arrangement of regenerator chambers built on an angle and having direct connection with the chimney. Waste heat boilers also form part of the equipment.

J. Hruska [9] prepared graphic curves showing results of many observations on the proper time of pouring large steel ingots.

The Blaw-Knox Company [10] has marketed a machine for repairing open hearth furnace slag lines. This does away with the arduous hand labor. It is said that the time required for making

[7] Am. Soc. Steel Treating, Handbook Sheets A-75 to A-84; 1926.
[8] Iron Age, 116: 675; 1925.
[9] Iron Age, 116: 1305; 1925.
[10] Iron Age, 116: 1673; 1925.

the back wall is seldom more than four or five minutes per furnace. It seems quite possible that the development of this machine may tend toward the design of wider hearths and better dimensional proportions than exists at present in the open hearth furnace.

The Rolling Mill.

A push bench process, also known as the Wellman-Peters process, has been devised for making seamless steel tubes.[11] The process consists in pressing a heated square billet into a hollow, thimble-shaped billet which is then passed over a mandrel and pushed through a series of reducing dies and a reeling or polishing machine.

A scraping device has been devised for cleaning billets and bars during the process of rolling.[12] Surface imperfections, such as heavy scale, scabs and slivers, are scraped off during the rolling process by means of vertical and horizontal knives.

Testing Instruments.

The Warner and Swasey Company of Cleveland has marketed a four wheel metallographic grinding and polishing machine with vertical spindles.

Albert Sauveur[13] described a newly devised machine known as the Sauveur Durometer for testing the hardness of steel and other metals by the measurement of the lateral rebound of a 10 mm. hardened steel ball falling vertically on the previously prepared surface of a test specimen which is set at an angle of 45°.

The Republic Flow Meters Company has marketed a new series of recording and indicating pyrometers. The notable features of these instruments are a high degree of accuracy combined with a simple but rugged construction and complete interchangeability of parts. Charles Engelhard and the Brown Instrument Company have also improved their recording pyrometers.

The Bausch and Lomb Optical Company and the E. Leitz Company have marketed new wide field binocular microscopes for the study of metal fractures and macrostructures as well as of foundry sands, ores and refractories. The instruments are fitted with paired eye-pieces and objectives.

[11] Iron Trade Rev., 77: 1079; 1925.
[12] Iron Age, 116: 1375; 1925.
[13] Trans. Am. Soc. Steel Treating, 9: 929; 1926.

Furnaces for the Heat Treatment of Steel.

A new electrically heated furnace for tempering hardened steel articles and involving a novel fan system for circulating the warm air in the furnace for the promotion of uniform temperature conditions, has been marketed under the name, "Homo" furnace. It was described by J. W. Harsch.[14]

The cost of heat treatment of steel depends on many other factors than the cost of furnace installation and the fuel, according to C. L. Ipsen.[15] He showed that the cost of fuel is often lower than that of any other single factor and demonstrated that the operating cycle must be the basis for any statement of the efficiency of a heat treating furnace. He also showed that the efficiency of electrically heated furnaces may vary anywhere from 33% to 78%, depending on the material to be heated and the operating cycle.

S. P. Rockwell has designed and placed on the market an apparatus for the heat treatment of steel by the "Volcrit" method. This involves the use of a special dilatometer which shows when the steel being heated has passed through its critical range by measuring the dilatation of the steel. O. E. Harder, R. L. Dowdell and A. C. Forsyth have described a similar method.[16]

Research on the Properties and Heat Treatment of Iron Base Alloys.

W. P. Sykes at the February, 1926, meeting of the American Institute of Mining and Metallurgical Engineers described original investigations on the iron-tungsten system. He published an equilibrium diagram of the iron-tungsten system.

E. C. Bain[17] describes the nature of the alloys of iron and chromium which involves the possible formation of a delta allotropic form of iron solid solution.

Dr. Albert Sauveur, at the February, 1926, meeting of the American Institute of Mining and Metallurgical Engineers, read a paper on "The Current Theories of Hardening of Steel, Thirty Years Later." This summarizes the condition of the hardening theories at that date and makes a critical study of the opinions of some twenty-four metallurgists representing the United States, Great Britain, France, Italy, Sweden and Japan, as to the nature

[14] Trans. Am. Soc. Steel Treating, 8: 340; 1925.
[15] Trans. Am. Soc. Steel Treating, 8: 36; 1925.
[16] Trans. Am. Soc. Steel Treating, 9: 403; 1926.
[17] Trans. Am. Soc. Steel Treating, 9: 9; 1926.

of martensite, the cause for its hardness, the conditions necessary for its formation and the mechanism of that formation.

M. A. Grossman and E. C. Bain [18] describe the nature of some low tungsten tool steels. The tests involved the measurement of their hardness, toughness, shrinkage and structural properties.

Howard Scott [19] investigated the dimensional changes accompanying the phenomena of tempering and aging tool steels. He showed that contraction with time is identified with the initial contraction on tempering, and expansion with the expansion on tempering which follows the initial contraction. He includes a list of seventeen references to other articles of interest in this connection.

A. H. Kingsbury [20] discusses the subject of tungsten steels used for cutting tools.

Jerome Strauss [21] discusses the cutting ability of tools and tool steels and the cutting resistance of metals. He points out general precautions necessary to be taken in the various methods of testing. He includes a selected bibliography of some thirty-three references on the subject.

W. L. Fink and E. D. Campbell [22] discuss the influence of heat treatment and carbon content on the structure of pure iron-carbon alloys. The experimental work included a rather complete study of the alloys with the X-ray Spectrometer and the article includes a selected bibliography of some seventy-nine references of interest.

C. B. Sawyer [23] reviews a large number of articles dealing with the effect of nitrogen in steel and gives conclusions from his own work on the subject.

H. J. French and T. G. Digges [24] experiment with the effect of nickel, tantalum, cobalt and molybdenum in high speed steels and conclude that any advantages gained by the addition of nickel and cobalt in such steels are associated with the heat treatment rather than the composition.

W. E. Ruder [25] shows that the magnetic permeability of crystals of silicon steel which have their cube edges perpendicular and parallel to the direction of the applied flux is from ten to twenty-

[18] Trans. Am. Soc. Steel Treating, 9: 259; 1926.
[19] Trans. Am. Soc. Steel Treating, 9: 277; 1926.
[20] Trans. Am. Soc. Steel Treating, 9: 597; 1926.
[21] Trans. Am. Soc. Steel Treating, 9: 571; 1926.
[22] Trans. Am. Soc. Steel Treating, 9: 717; 1926.
[23] Trans. Am. Soc. Steel Treating, 8: 291; 1925.
[24] Trans. Am. Soc. Steel Treating, 8: 681; 1925.
[25] Trans. Am. Soc. Steel Treating, 8: 23; 1925.

five times as great as that of crystals which have their cube edges at an angle.

Study of Magnet Steels.

J. A. Mathews[26] pointed out that according to his long experience, in the usual engineering alloy steels and high carbon steels, for all normal hardening mediums, austenite is always present with martensite; that in a wide variety of alloy steels, notably those capable of hardening readily in oil, there is more austenite retained after oil quenching than after the more common water quenching. He states that austenite is a cause of increased magnetic permanence or retentivity in those alloys capable of hardening readily in oil.

R. P. DeVries[27] points out from his study of several types of magnet steel for use in radio equipment that neither residual induction nor coercive force should be at a maximum but that a high average for both should be sought.

The Influence of Cold Work.

F. C. Langenberg[28] describes a process of manufacture by which the physical properties of large size, simple hollow cylinders, such as cast steel gun tubes, may be greatly increased over the usual properties obtained, by a special cold working process. He also studied the effect of the annealing operation on the elastic strength of cold worked simple and compound cylinders after the application of various kinds of cold working. For his paper he was awarded the Henry Marion Howe gold medal of the American Society for Steel Treating.

V. N. Krivobok[29] finds in cold worked steel a new critical point, similar to the usual critical points but opposite in sign, which he designates by the term "Ax." He expresses his belief that this point indicates both recrystallization and relief of internal strains and that its appearance must be closely connected with the specific properties imparted to a metal by cold working.

LIST OF SUGGESTED RESEARCH PROBLEMS.

1. The Physical Properties of Various Alloy Steel Castings.
2. The Application of Chromium Plating to Iron and Steel Objects.
3. Iron Base Alloys Which Will Resist Corrosion at High Temperatures.

[26] Trans. Am. Soc. Steel Treating, 8: 565; 1925.
[27] Trans. Am. Soc. Steel Treating, 8: 139; 1925.
[28] Trans. Am. Soc. Steel Treating, 8: 447; 1925.
[29] Trans. Am. Soc. Steel Treating, 8: 703; 1925.

4. Iron Base Alloys Which Will Resist High Pressures
5. The Effect of Adding Alloys to Cast Iron Castings.
6. A Short Test for Resistance to Fatigue.
7. Methods for the Beneficiation of Iron Ores.
8. A Study of New Alloy Structural Steels.
9. Further Study of Austenitic Iron Base Alloys.
10. The Application of Electric and Gas Welding to Structural Work for Buildings and Ships to Replace Riveting.
11. The Application of Electric and Gas Welding to Pressure Vessels.
12. The Nature of Iron Blast Furnace Slags.

Chapter V.

Lead.

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Prominence has recently been given to statements relating to the exhaustion of world resources of heavy metals. Such prospect has stimulated the application of chemistry to problems of increasing the supplies of lead, both by treatment of low grade and complex ores and by its recovery from waste materials and secondary metal. Chemistry is of particular importance in relation to lead, since more than half of the total production is converted to compounds of lead for use as paint, for storage battery manufacture, etc., the latter industry being now one of the largest single consumers of lead products.

Atomic Weights and Isotopes.

While the 1925 international atomic weight of lead is 207.20, Theo. W. Richards has reported this year that an exact determination on ordinary lead gives an atomic weight of 207.217. Lead has been shown to be the final decomposition product of uranium and of thorium, forming two distinct isotopes; the theoretical weight of the former being 206 (the atomic weight of uranium minus 8 atoms of helium), and the latter 208 (the atomic weight of thorium less 6 helium atoms). Lead has been found in nature closely corresponding to these two isotopes, namely, from South Dakota uraninite, with determined atomic weight of 206.071 and from Norwegian thorite with determined atomic weight of 207.77. An attempt by Richards [1] to fractionate mixed isotopes of lead with the use of ordinary lead was unsuccessful.

A very pure metallic lead has been made in the laboratories of the National Lead Company by the double electrolytic refining

* With the cooperation of W. A. Cowan and R. L. Hallett.
[1] J. Am. Chem. Soc., **48**: 1447; 1926.

of desilverized lead made from Southeast Missouri ores. A comparison of analysis is given here:

	Original	Twice Refined
Ag	0.0004%	Tr.
As	Tr.	Tr.
Sb	.0030%	0.00024%
Sn	None	None
Bi	.0030%	Tr.
Cu	.0003%	.00006%
Cd	None	None
Fe	.0015%	.00020%
Zn	Tr.	Tr.
Ni and Co	None	None
Mn	None	None
Total Impurities	0.0082%	0.00050%
Lead by dif.	99.9918	99.99950

One of the striking characteristics of this exceptionally pure lead is that its crystals are very large when cast under favorable conditions, indicating physical characteristics approaching those of single crystals.

Lead Ore Treatment.

The progress in the treatment of lead ores has been principally in connection with the so-called "complex ores" which contain minerals of lead and zinc (usually the sulfides) so closely associated that their separation by mechanical means is very difficult.

These ores are available in large quantities and the desirability of utilizing them has resulted in the invention and development of several special methods of treatment. The principal methods which are being tested at the present time are hydro-metallurgical processes, such as the Coolbaugh[2] and Christensen-Elmore processes, fire concentration and the application of selective flotation to ores of this kind.

The hydro-metallurgical processes are still in their experimental stages, and as yet it is hardly possible to predict what their future will be. In the Coolbaugh process the mixed sulfide ores are given a special roast to convert the zinc sulfide to sulfate, which is afterward leached from the ore with water or acid solution, leaving the lead in the residue. In the Christensen-Elmore

[2] U. S. P. 1,315,761; Sept. 9, 1919.

process, the mixed sulfide ores are treated with acid brine which selectively dissolves the lead mineral and leaves the zinc mineral. After the removal of one mineral the other may be treated by regular reduction methods.

When the complex ores of lead and zinc are treated by the fire concentration process, a commercially valuable leaded zinc oxide pigment is produced. This patented process makes use of a smelting furnace so operated as to volatilize most of the lead and zinc, which are caught in a dust collector in the form of the leaded zinc oxide pigment.

Selective flotation has become very important in the treatment of ores and great progress has been made during the past year. A number of improvements in flotation machines have affected the flotation results, but the greatest advance has been in the development of new flotation reagents and their use in special flotation circuits differing radically from older practice. These improvements in flotation have resulted in the production of zinc and lead flotation concentrates from the complex ores, which are of much higher grade than could be produced by the older practice.

During the year there has been some advance in the treatment of oxidized lead ores, both by flotation and special processes. Some success in the flotation of these ores has been obtained by chemical treatment which forms an artificial coating of lead sulfide on the particles of oxidized lead mineral and makes the particles amenable to flotation. One special process [3] agitates the finely ground oxidized lead ore with sponge iron in an electrolyte, reducing the lead to metal, in which form it responds to mechanical concentration.

Considerable progress has been made in the mechanical handling of ores, in improved roasting processes, in better operation of the mechanical Scotch hearth, in fume collection (bag houses becoming standard) and in the casting and handling of pig lead after casting.

It looks as though the softening of the more impure leads prior to desilverization would in the near future be almost entirely conducted by the Harris process, which consists in the oxidation of the impurities in the lead in a molten condition by circulating it through caustic alkali in the presence of a solid oxidizing agent which selectively removes the arsenic, tin and

[3] Wigton, U. S. P. 1,528,716; Mar. 3, 1925.

antimony with very little removal of lead. Dezincing is also accomplished by the Harris process.

It has been suggested that lead be softened under a bath of molten litharge, the litharge taking out the impurities, such as arsenic, antimony and tin. Desilverization continues according to the Parkes process. Electrolytic refining, including desilverization, according to the Betts process, still continues to be used. A suggestion has been made that sulfite lignose be used as an addition agent in electrolytic refining.

Impure hard, or antimonial lead, may be purified by the Harris process, giving a superior product. Considerable growth has taken place in the treatment of secondary lead containing tin for the removal of tin and other impurities, leaving the pure hard lead, and if the antimony is also removed, leaving pure soft lead.

White Lead.

The chemistry of white lead manufacture is very old, and there have been no radical departures within the past year, but continual improvements are made which tend to insure the uniformity and standard composition of the product.

Some of the scientific testing work in connection with white lead paint might be considered as an advance in chemistry of white lead, and of particular interest is the testing station at Sayville, L. I., where paints are tested by exposure to the weather on test panels, which are erected in such a way that they closely resemble building structures.

Because of the practical size and construction of the panels and also because of the practical manner in which the paint is applied, these tests while controlled with scientific accuracy give results closely comparable to practical painting work on buildings. In observing the results of paint on buildings, the history of the previous coats and even the exact information regarding the last job are usually difficult to obtain and in much testing work the panels are so small that the results are not practical. The Sayville Experiment Station combines the complete history and accurate scientific control with panels of such size and construction that the tests also have the greatest practical value.

Lead Oxides.

Progress has been made in the application of chemistry to the use of lead oxides in the manufacture of storage batteries,

of lead arsenate as insecticide and in the refining of petroleum products.

Powdered lead and mixtures of finely divided lead particles with oxides of lead have been proposed for paint to protect steel and for the manufacture of storage batteries. Special methods of preparation are claimed, one for the production of particles of colloidal size and another by Shimadzu [4] of Japan as producing lead suboxide (Pb_2O). However, a report by A. E. van Arkel [5] of the X-ray examination of so-called "lead suboxide" prepared from lead oxalate, states that it was found to be a mixture of lead particles and tetragonal red oxide.

Other investigations of lead oxides by X-ray diffraction methods have been reported for lead monoxide (PbO) and lead peroxide (PbO_2), while X-ray investigation of red lead (Pb_3O_4) has been only partially completed. The red and yellow polymorphous forms of lead monoxide have been shown by X-ray examination to differ fundamentally in structure (Kohlschutter and Scherrer [6]).

The U. S. Bureau of Mines has developed a method for the determination of metallic lead in the presence of lead oxide or other lead compounds. The latter are first dissolved by dilute solution of sodium hydroxide and the metallic lead is then attacked by silver nitrate.

Lead Alloys.

Advance in the study of lead alloys has been made in respect to effect of annealing or heat treatment on structure, the effect of pouring temperatures and in refining or separation of certain constituents by chemical methods.

Careful investigation of lead-antimony alloys showing the extent to which solid solution of antimony in lead occurs and the effect of heat treatment on this solid solution has been reported by R. S. Dean.[7] Heat treatment of this alloy results in great increase of hardness, as has been previously shown, both for lead-antimony alloys and for lead-tin alloys (L. Guillet [8]).

Alloys of lead with small amounts of other elements (introduced for the purpose of increasing hardness) have been investigated and used commercially, including those with small quanti-

[4] Brit. Patent 236,368; June 26, 1924. C. A., 20: 973; 1926.
[5] Rec. trav. chim., 44: 652; 1925.
[6] J. Soc. Chem. Ind., 43: 378B; 1924.
[7] Ind. Eng. Chem., 17: 1246; 1925.
[8] Compt. rend., 182: 1362; 1926.

ties of the alkali and alkaline earth metals and with antimony, tin and cadmium.

Continued investigation of high lead bronzes and lead-copper mixtures has been carried out with the purpose of preventing segregation; and the influence of lead and tin on certain brasses in respect to physical properties has been reported by D. Bunting.[9]

Lead Poisoning.

The Harvard Medical School,[10] supported by funds supplied by the lead industry, has made an exhaustive study of lead poisoning, laying a basis for scientific treatment. They have come to the conclusion that lead entering the respiratory tract, from which it cannot be removed except through entrance into the blood, is a greater cause of lead poisoning than lead entering the digestive tract, of which lead a large portion will normally be removed by excretion.

They find that lead may replace calcium in bone phosphate, and when so deposited has no effect upon the general health, although it may become dissolved should acidosis occur, and then produce symptoms of lead poisoning. This suggests a method of control still to be perfected, whereby the too rapid re-solution of lead from the bones can be prevented and a gradual re-solution and elimination can be secured.

In the prevention of lead poisoning it has been found in many cases that the use of waterproof sandpaper, that can be used in the wet or moist state, has been very effective because of prevention of dust.

The lead tetraethyl scare resulting from the death of a number of employees engaged in its manufacture has subsided, and it may be safely assumed that to the extent that lead tetraethyl is manufactured and used as an anti-knock compound, adequate precautions will be taken to prevent further calamity.

In summarizing the problems the lead industry is attempting to solve, we must give first place to the need of developing methods which will more effectively increase the supply of raw metal and methods which will provide for the better utilization of secondary metals. It seems as though these problems would be most easily solved by chemical methods.

While lead is recognized as one of the most valuable metals for use in the chemical industry, the growth of that industry is pre-

[9] J. Inst. Metals; 1925.

[10] Aub, Fairhall, Minot and Reznikoff, Lead Poisoning. William & Wilkins, Baltimore, 1926.

senting new problems, making the study of the corrosion of lead a subject of prime importance.

There are, of course, other problems connected with the lead industry relating to refinements of process, which it is unnecessary to touch upon here.

Chapter VI.

Magnesium.

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The most important present day uses for magnesium are: (1) Flash light powder and flares, (2) reagent in organic chemical synthesis, (3) deoxidizer and degasifier, (4) low percentage constituent in various types of alloys, (5) magnesium base alloys both for castings and mechanically worked parts. Some activity is manifest in the first four fields, but the keenest interest now centers around the development of magnesium base alloys for aëronautics and similar fields.

Production.

Magnesium is commercially obtained by the chloride and oxide processes.[1, 2, 3, 4] Recent improvements in production technique consist in the Bakken[5] method of separating magnesium from the cell by vaporization under reduced pressure, followed by subsequent condensation; and also in the Cottringer and Heath[6] method of utilizing the hydrated forms of magnesium chloride, by introducing the same into the cell bath adjacent to the anode.

Tonnage production, of course, is low as compared to aluminum. However, the price ratio is constantly becoming more favorable. Magnesium 99.8-99.9% is quoted at 75 cents per pound in ton lots, which is equivalent to about 47 cents per pound when compared to aluminum, volume for volume. It can be purchased at a lower price than this in larger quantities and increased production and improvements in technique are gradually lowering the cost.

[1] Daniels, Mech. Eng., 47: 796; 1925.
[2] Harvey, Chem. Met. Eng., 32: 573; 1925.
[3] Miyake and Bults, Eng. Min. Press., 119: 843; 1925.
[4] Anderson, in Liddell, Handbook of Non-Ferrous Metallurgy, Chapter XX. 1926.
[5] U. S. P. 1,584,689; 1925.
[6] U. S. P. 1,567,318; 1925.

Foundry Practice.

The most recent discussions on foundry practice are those of Daniels,[1] Anderson,[4] and Schmidt.[7] The patent literature discloses many recent improvements. Bakken[8] advocates melting the metal in the absence of active gases with the introduction of glycerine over the metal prior to casting. Schreiber and Beck[9] use sulfur to protect the metal during the melting operation. Burdick and Veazey[10] employ a flux while melting and alloying, and Gann[11] discloses improvements in the composition and preparation of suitable fluxes. The use of sulfur, boric acid, glycerine, and water glass in molding sand to prevent burning of the magnesium during the casting operations has been disclosed by Beck,[12] Osborne,[13] and Wilhelmy[14] respectively.

Processes for recovering magnesium alloy shavings and scrap have been described by Hess,[15] Beielstein,[16] and Beck.[17] Rhodin[18] has patented the extraction of magnesium from magnesium-zinc alloys by treating the same with molten alkali.

Magnesium Base Alloys.

The constantly increasing importance of magnesium base alloys is largely due to their extreme lightness coupled with good strength and toughness. This ratio, as expressed by specific tenacity, and the fatigue endurance are so favorable that in this respect, certain magnesium alloys surpass most other metals. This particular combination of properties makes these alloys especially suited for aircraft construction and automotive parts. As a result these alloys are being extensively studied and practical uses sought. Some of the more important applications thus far made are: superchargers, crank cases, air-cooled cylinders, reciprocating parts, instrument housings, fuselages, propeller blades, and rolled sheet metal for airplanes, together with reciprocating parts, crank cases, and horn resonator discs, and other automotive accessories.

Other valuable features of magnesium base alloys are the wide

[7] Schmidt, Met. Ind. (London), 28: 130; 1926.
[8] U. S. P. 1,555,956; 1925.
[9] U. S. P. 1,540,867; 1925
[10] U. S. P. 1,558,066; 1925.
[11] U. S. P. 1,519,128; 1924. 1,534,105; 1925.
[12] U. S. P. 1,463.609; 1923. 1,584,072; 1926.
[13] U. S. P. 1,533,892; 1925.
[14] U. S. P. 1,544 710; 1925.
[15] U. S. P. 1,519,204; 1924.
[16] U. S. P. 1,524,470; 1925.
[17] U. S. P. 1,576,080; 1926.
[18] U. S. P. 1,539,955; 1925.

range of mechanical properties that can be obtained by varying the chemical composition and treatment. These alloys are furthermore characterized by the ease and speed with which they can be machined. There is no tendency to tear and smear over, very little dulling of the cutting tool, and no cutting compound is required. These factors very materially reduce the cost of machined articles.

The more important summaries of the physical and mechanical properties of magnesium alloys are given by Archbutt,[19] Daniels,[1] Moore,[20] Schmidt [7] and Gann.[21] The general characteristics of some of these alloys are summarized in the following tables which give approximate values only.

TABLE I.

Cast Magnesium Alloys.

Composition	Ultimate Strength lb./sq. in.	Load ½% Elong.	Per Cent Elong.	Specific Gravity	Fatigue Endurance Limit— lb./sq. in.	Specific Tenacity
Pure Magnesium..	14,000	4,000	5.4	1.74	.....	8,000
Mg 98–Al 2.....	24,000	7,000	10.1	1.75	.....	14,000
Mg 96–Al 4.....	26,000	9,500	8.4	1.76	.....	15,000
Mg 94–Al 6.....	28,000	10,500	7.4	1.78	.....	16,000
Mg 92–Al 8.....	25,000	13,000	4.0	1.80	12,500	14,000
Mg 90–Al 10.....	22,000	14,500	2.0	1.82	.....	12,000
Mg 88–Al 12.....	21,000	17,000	1.2	1.84	.....	11,000
Electron AZ	24,000	.....	5.0	1.83	.....	13,000

PROBLEMS.

All phases of the magnesium industry are worthy of further investigation. Some of these problems are chiefly of scientific interest, while others are more closely related to commercial practice.

The literature is full of references to the use of magnesium and magnesium alloys as deoxidizers and degasifiers. In certain problems, such as nickel refining, the superiority of magnesium is unquestioned. While indications are favorable with other metals, a considerable amount of work is necessary to determine the best operating technique.

The addition of small amounts of magnesium are known to improve the properties of certain alloys, particularly those of aluminum. Other classes of alloys have not been so thoroughly investigated, and the claims of certain investigators have not been substantiated by others This likewise holds for the aluminum alloys of the magnalium type.

[19] Metallurgist (Suppl. to Engineer), 2: 4, 26; 1926.
[20] Proc. Am. Soc. Test. Mat., 23 II: 107; 1923. 24 II: 547; 1924. 25 II: 67; 1925.
[21] Trans. Am. Soc. Steel Treating, 2: 607; 1922.

TABLE II.

Wrought Magnesium Alloy.

Composition	Ultimate Strength lb./sq. in.	Proportional Limit	Per Cent Elong.	Specific Gravity	Fatigue Endurance Limit—lb./sq. in.	Specific Tenacity
Pure Magnesium..	29,000	1,100	6.0	1.74	8,000	16,700
Mg 98–Al 2.....	.....	.....	...	...	.....	.....
Mg 96–Al 4.....	36,000	3,000	20.0	1.76	12,000	20,500
Mg 95.8–Al 4–Mn 0.2	39,000	13,500	15.5	1.77	15,000	22,000
Mg 94–Al 6.....	41,000	5,500	16.0	1.78	13,000	23,000
Mg 92–Al 8.....	46,000	10,500	9.0	1.80	14,000	25,500
Mg 90–Al 10.....	47,000	7,000	8.0	1.82	.....	26,000
Mg 88–Al 12.....	45,000	10,500	7.5	1.84	.....	24,500
Mg 92.8–Al 7–Mn 0.2	44,000	15,000	14.0	1.79	15,000	24,500
Mg 95.6–Zn 4.4...	36,500	6,000	17.5	1.78	17,000	20,500
Mg 90–Cu 10.....	39,000	14,000	3.0	1.90	11,000	26,000

A method for the microscopic identification of the various components of magnesium alloys should be worked out similar to that now existing for steel, aluminum alloys, etc.

Many of the magnesium alloy constitutional diagrams are questionable as to accuracy. This is well illustrated by recent investigations on the magnesium-aluminum series. The accurate construction of other constitutional diagrams would be of great service as a guide in helping to disclose which magnesium alloy compositions would have desirable combinations of properties.

Chapter VII.

Nickel.

Paul D. Merica,

Director of Research, The International Nickel Company.

The major part of the world's production of nickel is used industrially in metallic forms—steel, alloys, castings, nickel-plating, etc. Perhaps 5% is used in other chemical forms, principally in the Edison storage cell and in the catalysis of oil hydrogenation. It is not surprising that current history of nickel largely concerns metallurgical rather than chemical developments.

Nickel Refining.

Although refinements are constantly being made in the mining, smelting and refining operations of nickel production, in the direction both of lowering production cost and of improving quality of product, no fundamental changes in the three established processes are being undertaken. New nickel products are being brought out from time to time by the producers, principal among the recent ones being a high purity electrolytic nickel and a low-melting-point nickel for alloying purposes (for cast iron).

Nickel Cast Iron.

It is safe to say that the focus of interest in nickel today lies in the development and diversification of its commercial utilization.

One of the newest and most active developments of the industrial use of nickel is that of nickel cast iron. Although there had been isolated prior references to nickel in cast iron and indeed even some industrial use of it before 1925, our systematic knowledge of this subject may fairly be said to date from the presentation, in September, 1925, of a paper by Wickenden and Vanick [1] on "Nickel and Nickel-Chromium Cast Iron". Since

[1] Transactions A. F. A.; 1925.

then development of this new use for nickel has been proceeding fairly rapidly.

Metallurgically, nickel refines the grain of gray cast iron and increases its hardness and wear-resistance without, however, impairing its machinability. Its principal value in the iron foundry is due to these effects; with nickel gray iron may be produced with a greater "machinable hardness" than without. Its established industrial uses now include such castings as automobile, pump, compressor, steam, Diesel engine cylinders, sleeves and liners, pistons and piston rings, gears, cams, rolls, forming dies, machine tool tables and benches, resistance grids, etc.

Electrodeposition of Nickel.

In recent years the art of electroplating has been undergoing continuous improvement as a result principally of the application of scientific principles of operation and control.

Nickel-plating has been sharing generously in this progress. As a result of the investigations of Blum and co-workers,[2] Watts,[3] Thompson,[4] Mudge,[5] Pedersen,[6] Madsen,[7] and others our knowledge of the different features of the nickel-plating process has been greatly enlarged and intensified. We know today how to control the operations of cleaning and of plating, know within what limits of hydrogen ion-concentration and chemical composition plating solutions must be held, recognize better the origin of many of the troublesome plating defects. Commercial plating shops are rapidly taking advantage of the newer ideas and are producing substantially better nickel-plating. Many shops are going further and by using heavier nickel deposits [8] are securing a high degree of surface permanence and rust-resistance of plated steel articles even when exposed out-of-doors.

Alloys for High Temperature Service.

The use of that group of alloys somewhat loosely called "heat-resistant" is rapidly increasing, particularly in annealing and heating furnaces in the steel industry, in roasting furnaces, in chemical equipment for high temperature operation, coal-carbonization,

[2] Trans. Am. Electrochem. Soc., **48**: 69; 1925.
[3] Trans. Am. Electrochem. Soc., **48**: 31; 1925.
[4] Trans. Am. Electrochem. Soc., **47**: 163; 1925.
[5] Trans. Am. Electrochem. Soc., **47**: 137; 1925.
[6] U. S. P. 1,564,710; Dec. 8, 1925.
[7] U. S. P. 1,583,891; May 11, 1925. U. S. P. 1,584,959; May 18, 1926. U. S. P. 1,513,119; Oct. 28, 1924.
[8] E. M. Baker, J. Soc. Automotive Eng., **14**: 127; 1924.

etc. No fundamental changes have taken place recently in the types of alloys used (principally nickel-chromium-iron alloys). It is interesting to note briefly the pertinent properties of some of these alloys.[9]

	Rate of Oxidation in Air at 1000° C.	Safe Working Stress at 1000° C.
Steel	0.250″ in 2 wks.	200 psi
Nickel-chromium-iron alloy	.001″ in 2 wks.	1500 psi

The tremendous advantage of the nickel-chromium-iron alloys over steel for structures exposed to high temperatures is apparent.

Nickel Steels.

One of the principal uses for nickel is in the well-known nickel steels. This is such a broad and ever-changing field that mention only can be made of new developments.

By reason of its remarkable wear-resistance under heavy pressures 5% nickel steel is being increasingly used for case-hardening work particularly in the automotive field; for rear-axle and transmission gears, etc.

The Timken Roller Bearing Company has developed the use of a 1.50% nickel, 0.25% molybdenum steel for roller bearings as an improvement over the older chromium steel bearings.

A most interesting and important development is the recent rolling of 3.0% nickel steel boiler plate by the Lukens Steel Company for Canadian Pacific Railroad locomotives. The use of the nickel steel plate with its higher physical properties (70,000 psi tensile strength specified) will permit the use of 250 pounds boiler pressure instead of the 200 pounds standard pressure with ordinary plate, with proportionate gain in tractive power.

Corrosion-Resistant Alloys.

Nickel is used in a number of corrosion-resistant alloys in current industrial use.

The use of Monel metal equipment has been gradually extending into the semi-chemical fields such as dyeing, laundering, pickling, drying, as well as in the food industries—packing, canning, restaurant, hotel, refrigerator.

[9] Fahrenwald, Proc. Am. Soc. Testing Materials, 24: 310; 1924.

A series of nickel-chromium-iron alloys is known exhibiting substantial corrosion-resistance. Typical compositions are:

	Nickel	Chromium	Iron
(1)	22%	8%	Balance
(2)	12	16	"
(3)	8	18	"
(4)	7	20	"

These materials all have similar properties, being moderately hard, machinable and readily fabricated in sheet or rod form. Number 1 is used in this country, Nos. 2 and 3 principally in England and No. 4 in Germany, for valves, pump rods and plungers, marine shafting, pump impellers, shafting, corrosion-resisting bolts, nuts, screws, fan blades and blowers, tanks, conveyor buckets, etc.[10]

Pure, malleable nickel is also making a place for itself in certain, semi-chemical fields, particularly for equipment used in the handling, pasteurizing and treatment of milk and other dairy products. The use of this material in chemical equipment has been greatly aided by the recent appearance of seamless nickel tubing on the market.

PROBLEMS.

There are three fields in which it would seem that further investigational work would yield valuable results both from practical and theoretical standpoints.

Nickel affects the structure and properties of cast iron in quite an unusual manner; *i.e.*, it reduces size of graphite flake, hardens the matrix while at same time reducing combined carbon. No other method is known by which these properties may be simultaneously so affected. This remarkable contrast affords thus an admirable opportunity of securing more information regarding the genesis of gray cast iron structure; information which in turn might permit us to improve gray iron considerably in strength, hardness and machinability.

The addition of small amounts of nickel is known to improve the properties of certain cast bronzes, and indeed nickel may be advantageously substituted for the more expensive element, tin, to a certain extent in them. Yet our knowledge of the ternary equilibrium of the copper-nickel-tin alloys is practically nil. A thorough investigation of this system would be of considerable benefit to the brass foundry industry.

The ferro-nickel alloys have been the subject of innumerable investigations dating from Faraday. Yet even today there is a considerable uncer-

[10] Monypenny, Stainless Iron and Steel, Wiley, 1926. Development of Staybrite Steel, Thos. Firth & Sons., 1926.

tainty as to the nature of the transformations in these alloys and the effect of carbon and chromium on them. What is the nature of the so-called reversible (magnetic) transformation—is it purely an electronic one? Why is the irreversible transformation so sluggish and yet so difficult to suppress even by rapid cooling? A more complete understanding of the behavior of this series of alloys would represent a considerable advance in our general metallurgical education.

PROPOSED RESEARCHES ON NON-FERROUS METALS

[The Institute of Metals Division Research Committee of the American Institute of Mining and Metallurgical Engineers, through its chairman, Paul D. Merica, announces the preparation of two lists of fundamental technical problems on Non-ferrous Metals. The first list comprises six selected problems: Solubility of lead in brass and the effect of lead on the alpha-beta solubility curves of brass diagram; Iron zinc equilibrium diagram; The joining of metals; The high temperature chemistry of metals and alloys with particular reference to gases; The influence of varying quantities of aluminum on non-ferrous alloys subject to hydrostatic tests; Silver alloys. The second list contains twenty-four problems. Mimeographed copies of these lists, which include a general discussion of the problems by the men who proposed them, may be obtained from the following: Paul D. Merica, The International Nickel Company, 67 Wall Street, New York City; The Research Information Service, National Research Council, B and 21st Streets, N. W., Washington, D. C.; The Secretary, American Institute of Mining and Metallurgical Engineers, 29 West 39th Street, New York City.]

Chapter VIII.

Radium and Radioactivity.

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Research directly in the field of radioactivity has not been very active in the United States during the past few years. Many of the original pioneers have turned their attention in other directions, while different branches of subatomics have attracted the newer workers.

The same state of inactivity exists in research related to radium production. With the passage of supremacy in the radium industry to the Belgian Company "Radium Belge", the volume of industrial radium research in this country has been reduced almost to nothing.

There are, however, certain allied fields involving radioactive substances and principles in which work has been carried on with considerable vigor. For example, the determination of the age of uranium and thorium minerals by means of their radioactive accumulations has been stimulated through the efforts of the Committee of the National Research Council on the Age of the Earth by Atomic Disintegration, with the production of results interesting to geologists, radioactivists and chemists alike.

C. W. Davis [1] made a complete analysis of three uranium minerals from Katanga (Belgian Congo), from South Dakota and from Utah. From the Pb/U ratio, he estimated the ages, on the assumption that all the lead found was of radioactive origin. The age calculated for the uraninite from South Dakota (Keystone) was the greatest yet claimed for any uranium mineral, 1667 million years. It was therefore of the greatest importance to know whether all the lead was really Ur-Pb. This point was settled very conclusively by Richards and Hall [2] who found

[1] Am. J. Sci. (v), 11: 201; 1926.
[2] J. Am. Chem. Soc., 48: 704; 1926.

for lead from the same source an atomic weight of only 206.02.

In the same connection should be mentioned the earlier work of Richards and Putzeys,[3] who obtained an atomic weight of only 206.2 for lead from a mixture of secondary Pb-U minerals from Katanga. They concluded that the lead, which formed an integral part of the lead-uranium compounds constituting the new minerals, was chiefly U-Pb. Hönigschmidt got the same result independently. This means that we have cases where, in spite of the radioactive origin of the lead, it cannot serve as an age index, because the Pb/U ratio has been disturbed, in that case increased, by transport and new association with uranium, not in the true age ratio but in chemical proportions. This must raise the question as to how far or under what circumstances one can rely on the radioactive ratios as a measure of age.

The gases collected by Davis from the same uranium minerals were also analyzed. The association disclosed between helium and the other gases led Lind [4] to conclude that the original chemical effects of the parent α-particles acting within the mineral, might be of considerable consequence in the generation of gases like oxygen and nitrogen and in their influence upon the migration and liberation of helium into the atmosphere. David White [5] suggested that the oxygen of the atmosphere might have originated within the earth's crust from the decomposition of water by α-particles.

Among the physical effects of radium radiation the studies of Miss Rodman [6] on the effect of temperature on the luminosity of radium compounds formed an important extension of earlier work by Karrer and Kabakjian.

In a series of papers by Lind and Bardwell [7] and their coworkers, the chemical reactions produced by α-rays were measured for a number of organic and inorganic reactions and the effects were related to the ionization. The hydrocarbon homologues (methane to butane) were found to behave alike in splitting out hydrogen from a bi-molecular complex to produce higher members, even liquids and solids. The oxidation of methane and of ethane by oxygen was found to be regular and complete to carbon dioxide and water. Butane, however, gave liquid partial

[3] J. Am. Chem. Soc., 45: 2954; 1923.
[4] Proc. Nat. Acad. Sci., 11: 772; 1925.
[5] J. Wash. Acad. Sci., 15: 423; 1925.
[6] Phys. Rev., 23: 478; 1924.
[7] J. Am. Chem. Soc., 47: 2675; 1925. 48: 1556, 1575, 2335; 1926.

oxidation products, only one molecule of butane reacting with one of oxygen; while the oxidation of propane was only partially complete. The unsaturated compounds, like acetylene, cyanogen, and ethylene, were found to have a high power of condensing (20, 7 and 5 molecules respectively per ion-pair), the two former giving solid products while ethylene gave a liquid product. It was also found that gases inert to the reactions being caused by α-radiation, nevertheless accelerated them in proportion to the additional ionization of the inert.

In a paper by Porter, Bardwell and Lind [8] the effects of light and of α-radiation in causing combination of hydrogen and chlorine were compared. It was found that at 25° one ion-pair is twice as effective as one quantum of (blue) light in initiating the chain reaction; while at 100° they become equal in efficiency. The length of chain is the same in both cases for equal sensitivity which may be changed through almost any range by controlling the quantity of inhibitor present.

Opportunities for further research in radioactivity and allied subjects are especially good. The field was originally explored with great rapidity in mapping out its broader features. The general framework was established by finding interlinking supports, which did not require great accuracy in the values of some of the separate units entering into the structure. Many of these lacunæ have since been filled by data of sufficient precision. But some of the very important constants are not yet known with an accuracy better than 10%.

In the related fields, there is the greatest need for further work; in geology, for example, in determining the ratio of the different parent and end members in various radioactive minerals from different localities. Research of this character may be expected to throw light not only on the age relations, but on the genetic problems of the radioactive families themselves. For example, the relation of the actinium to the uranium family is not yet definitely known. Even so fundamental a question as the genetic independence of the uranium and thorium families has been raised [9] and can be settled only by further work of the character under consideration.

In radioactivity itself, the number of alpha particles emitted by one gram of radium per second is still in doubt over a range of

[8] J. Am. Chem. Soc., 48: 2603; 1926.
[9] G. Kirsch, Inst. f. Radiumforsch., Mitt. 150. Sitzb. Akad. Wiss. Wien., 1922.

8%. The number of ions produced by one alpha particle is subject to question within limits almost as wide. The opportunities to use radioactive materials in studying various physical-chemical properties far outside the usual experimental limits of concentration have not begun to be exhausted or even widely employed. The geochemical effects of radium radiation are not known either in the atmosphere or in the earth's crust, though we have given some indication that they may be very important.

In purely physical problems, the mass of the ions produced in different gases by alpha, beta and gamma radiation awaits investigation.

The progress made in the quarter of a century elapsed since the discovery of radium is truly stupendous. Nevertheless the vast possibilities disclosed have only begun to be realized. The work has been shared in by chemists and physicists alike. Both have encountered new problems of technique and of materials; both, but especially the physicists, have had simultaneously before them several other remarkably fruitful fields for investigation. In short, we find ourselves in one of the most active periods of the progress of the physical sciences where the impetus of the new discoveries and further opportunities will last for at least a generation.

Aside from research, it may be profitable to consider what new didactic possibilities are presented and how they are being taken advantage of. Radioactivity in its present state of development is a highly systematic, non-mathematical subject which stimulates the imagination of various classes of students and hence can be readily presented. The new facts are being adequately taught to advanced students of chemistry, and much progress has been made in introducing some of the elements into beginning courses. Much more can be done in this latter direction, with the double advantage of presenting the atom as a fact rather than a theory, and in furnishing a more definite and tangible basis for the periodic system. Even in advanced work, there are many unutilized opportunities to introduce the principles of radioactivity. For example, radioactive changes represent the most perfect examples of first order reaction that we have. Some of them can be easily measured and at least one should be introduced into every laboratory course in physical chemistry as one of the regular experiments in velocity of reaction, which would also illustrate the principles and simpler technique of radioactive measurements.

Chapter IX.

The Rare Earths.

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The elements known as the "Rare Earths", so named originally because of their scarcity, are so closely related both chemically and physically that exact knowledge concerning them has been developed very slowly during the century and a quarter that has elapsed since the discovery of this group.

Each new means of investigation when applied to these elements has resulted in the broadening of our knowledge. Fractional precipitation and fractional crystallization with various reagents, the spectroscope applied both to the arc and the absorption spectrum, have increased our knowledge until instead of one element we later came to recognize a dozen or more elementary substances.

Classification according to atomic numbers revealed a gap which previous investigators have not filled. Refinements in study due to the development of the X-ray spectroscope have resulted in the further broadening of our knowledge of these elements. Careful and systematic investigation convinced B. Smith Hopkins [1] of the University of Illinois that he had identified a previously undiscovered element with an atomic number of 61, thus supplying the missing link between neodymium (60) and samarium (62).

The concentration and isolation of this new element, named by its discoverer illinium (Il) after the state and university where the discovery was made, was effected by a long series of fractional crystallizations first as double magnesium nitrates and then as bromates. It was identified by means of the X-ray spectroscope and the systematic use of this apparatus enabled the discoverer to study and control his chemical separations. The investigations on this new element are being vigorously prosecuted with larger

[1] J. Am. Chem. Soc., 48: 1585; 1926. Phys. Rev., 25: 106; 1925.

quantities of rare earth material and further announcements are awaited with interest.

The elements masurium (43) and rhenium (75), the discovery of which was reported last year by Noddak and Tacke,[2] have been further investigated by the discoverers and their physical and chemical properties, including their X-ray spectra, described. They are probably present in platinum ores and in columbite.

The history of the work on these two elements and the methods of X-ray spectroscopy were described at length by Ernst Rüst.[3]

Hafnium, discovered by Coster and Hevesy a year or more ago, has been the subject of continued investigation and the discoverers, with other investigators, have obtained patents for processes of separation from zirconium.[4]

G. Hevesy [5] has given a detailed report of their investigations, including a description of the properties of the element.

Hönigschmidt and Zintl,[6] working on material supplied by Hevesy and Jantzen after 5000 crystallizations of the zirconium-hafnium mixture, have given the atomic weight of hafnium as 178.6.

Henning [7] has determined the melting point of hafnium oxide (HfO_2) as 3085° ± 25° abs., while ZrO_2 melts at 2960° ± 20° abs. The properties of various hafnium compounds are being systematically investigated by a number of chemists throughout the world.[8]

Although zirconium has long been known, the chemical and physical properties of its oxide and salts have been the principal object of investigation until rather recently when the metallurgical properties of the element and particularly its alloys have come into consideration. F. M. Becket and A. L. Field [9] state that a heat-treated carbon steel containing zirconium has higher ductility than steels of comparable strength and hardness that contain no zirconium. They [10] also specify an alloy-steel hardened by heat treatment that contains zirconium, chromium, tungsten, vanadium, molybdenum or manganese.

[2] Oesterr. Chem. Ztg., 28: 127; 1925. Sitzb. preuss. Akad. Wiss., 1925: 400.
[3] Tech. Ind. Schweis. Chem. Ztg., 1925: 234.
[4] U. S. P. 1,582,860; Apr. 27, 1926. U. S. P. 1,586,241; May 25, 1926. Brit. Pat. 235,217; June 16, 1924. Brit. Pat. 238,543; Aug. 13, 1924.
[5] Chem. Reviews, 2: 1; 1925. Kgl. Danske Videnskab. Selskab. 6, No. 7: 4; 1926.
[6] Ber., 58B: 452; 1925.
[7] Naturwissenschaften, 13: 661; 1925.
[8] J. Am. Chem. Soc., 47: 2540; 1925. Z. anorg. allgem. Chem., 144: 69; 1925. Z. anorg. allgem. Chem., 150: 210; 1926.
[9] U. S. P. 1,550,489; Aug. 18, 1925.
[10] U. S. P. 1,550,490; Aug. 18, 1925.

Becket [11] also adds zirconium to a steel of high phosphorus content to counteract the effect of the phosphorus and increase the Izod impact number. Ferro-zirconium alloy is prepared by R. H. McKee [12] by fusing an oxide compound of zirconium (*e.g.*, ZrO_2) with a metallic sulfide such as FeS and removing the S by blasting. A pyrophoric alloy, suitable for igniters, consisting of zirconium and 20-40% tin, has been produced by H. S. Cooper.[13] J. W. Marden and C. C. Van Voorhis [14] have developed a method of preparing zirconium by heating together the oxide (ZrO_2) and an alkali metal like sodium and an alkali or alkali metal halide, the base of which is different from the alkali metal used (*e.g.*, $BaCl_2$ in absence of O or N), and this process may be applied to other refractory metals. J. H. de Boer and J. D. Fast [15] have prepared pure zirconium by the thermal decomposition of the iodide, obtaining a ductile metal with a sp. gr. of 6.5 and a m. p. of 2200° abs. Zirconium oxide is finding steadily increasing use as an opacifier in enamels; [16] it is also being used in the manufacture of crucibles, etc., for high temperature work in the electric furnace.[17]

It also enters into the composition of some glasses resistant to sudden temperature changes.[18]

New methods of separation and a number of new zirconium compounds have been described.[19]

Thorium finds its chief industrial application in the Welsbach incandescent gas mantle and, strange as it may seem, in the electric lamp filament also, where it plays a part quite out of proportion to the small percentage present, being an essential component of ductile tungsten filaments.[20] It is found to be equally useful in the filaments of the wireless bulbs.

During the year in the study of catalytic agents Wm. W. Russell and H. S. Taylor [21] have demonstrated that thoria (ThO_2) acts as a "promoter" when used in connection with nickel catalysts, the theory being that its primary function is to make possible the

[11] U. S. P. 1,546,881; July 21, 1925.
[12] U. S. P. 1,565,280; Dec. 15, 1925.
[13] U. S. P. 1,562,540; Nov. 24, 1925.
[14] U. S. P. 1,573,083; Feb. 16, 1926.
[15] Z. anorg. allgem. Chem., 153: 1; 1926
[16] C. J. Kinzie, U. S. P. 1,562,890; Nov. 24, 1925. U. S. P. 1,588,476; June 15, 1926.
[17] Rev. Chim. Ind., 35: 14; 1926. Rev. Universelle Mines (7), 7: 218; 1925.
[18] Horak, U. S. P. 1,557,540; Oct. 13, 1925.
[19] Windsor, J. Am. Chem. Soc., 48: 310; 1926. de Boer, Z. anorg. allgem. Chem., 144: 190; 1925. Hartmann, U. S. P. 1,576,275; Mar. 9, 1926. de Boer and van Arkel, Z. anorg. allgem. Chem., 148: 84; 1925. Prideaux and Roper, J. Chem. Soc., 1926: 898.
[20] General Electric Co., Ltd., Brit. Pat. 233,294; May 3, 1924.
[21] J. Phys. Chem., 29: 1325; 1925.

existence of a greater number of nickel atoms of a highly unsaturated character.

G. R. Levi [22] has studied seven different varieties of thoria and found that all were apparently equally energetic catalytic agents in the dehydration of alcohol. Thoria, on account of its high melting point and its chemical inertness, is finding an increasing application in the preparation of high temperature refractories, particularly since Fairchild and Peters [23] have succeeded in fusing it to a transparent glass. It is anticipated that thoria will eventually find an extensive use in connection with the electric furnace.

Cerium is an essential component of the Welsbach mantle, although to only approximately 1% of the thoria present. The quantity consumed in this industry is not large, although a substantial tonnage is made available as a secondary product in the production of thoria from monazite sand.

Some of this finds a market in the production of special grades of glass,[24] while the manufacture of electrodes for white arc electric lamps creates a demand for a considerable quantity of this element.

Cerium in admixture with lanthanum, neodymium, etc., has for many years found rather extensive use in medicine in the form of oxalates, where it acts to prevent nausea in stomach troubles.

It is now found [25] that cerium-iodine compounds are effective in the therapy of tumors—particularly those of the lymphogranuloma type. The cerium seems to be the effective agent with the iodine serving merely as an activator. A recent application of this rare earth mixture is in rendering vegetable fabrics both mildew-proof and water-repellant.[26] The production of ferrocerium or pyrophoric alloy utilizes a fair quantity of cerium,[27] although in a crude form. K. Swoboda and R. Horny [28] have developed a method of analytically determining the cerium in this alloy, while L. Fernandez [29] has developed an extremely sensitive test for this element, said to indicate the presence of as small a quantity as one part in five million.

Lanthanum, neodymium, praseodymium and samarium, the other

[22] Atti Accad. Lincei (6), **2**: 419; 1925.
[23] U. S. P. 1,545,951; July 14, 1925.
[24] Japan Ceram. Assoc., **32**: 91; 1924.
[25] Lewin, Med. Klin., **20**: 1317; 1924.
[26] White, U. S. P. 1,536,254; May 5, 1925.
[27] Geay, Rev. Chim. Ind., **34**: 302; 1925.
[28] Z. anal. Chem., **67**: 386; 1926.
[29] Gazz. Chim. Ital., **55**: 616; 1925.

elements of the cerite group, have for many years been studied by chemists throughout the world and this year is no exception. The properties of various salts have been studied and the literature records the results of these investigations. No new industrial use has been developed and the only one of these elements that is in use industrially is neodymium which is employed in certain grades of optical glass, particularly some of the Crookes' lenses.

Wierda and Kremers [30] have investigated the properties of pure praseodymium element and find it to be a silvery white metal which corrodes rapidly in the air, is slightly attacked by hot water and is vigorously attacked by mineral acids and free halogens. The kindling temperature is 290° and the metal is not pyrophoric. The Brinnell hardness (500 kg. wt.) is 25, sp. gr. 6.60 (25°) and m. p. 940° (Muthmann). Alloys with most common metals form readily.

Jas. Kendall and B. L. Clarke [31] have successfully applied their previously described ionic migration method to the separation of yttrium and erbium, neodymium and praseodymium, and gadolinium and samarium.

The very rare element germanium, although not classified among the "rare earths," has been systematically investigated by L. M. Dennis and his co-workers [32] at Cornell University. These papers are part of a series of publications from this laboratory on this subject.

Much painstaking investigation will still be required before our knowledge of these newly discovered elements is any way complete and even the better known elements still give opportunity for original research. With more complete information some practical use for these unutilized elements will doubtless result.

The general fields of metallurgy, ceramics and medicine seem to offer especial encouragement for successful applications of the elements of this very interesting group. They also seem to be well suited as special catalysts and the entire subject furnishes a strong appeal to research investigators throughout the world.

[30] Trans. Am. Electrochem. Soc., **48**: 159; 1925.
[31] Proc. Nat. Acad. Sci., **11**: 393; 1925.
[32] J. Am. Chem. Soc., **47**: 1945, 2039; 1925. J. Phys. Chem., **30**: 1043, 1047, 1049, 1055; 1926.

Chapter X.

Zinc and Cadmium.

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The major part of the world's production of zinc is used industrially in metallic forms. A minor part is used in the forms of oxide, chloride and sulfate, which are to a considerable extent derived directly from ore, to a considerable extent from metal scrap, junk, and metallurgical between-products, and to a certain extent from the use of refined virgin metal.

The metallic forms in which zinc is used are spelter and dust. Spelter, which is the metallurgical term for the commercial metal, is distinguished as common and high-grade, which may almost be viewed as two different metals.

Common spelter is an alloy of about 98.5% zinc, with 1% lead, a varying proportion of cadmium, and a few hundredths % of iron and other impurities. High-grade spelter contains about 99.95% zinc, and consequently in its refinement is analogous to that of commercial copper and lead. High-grade spelter is distinctly softer than common spelter and is capable of numerous uses to which common spelter is not at all adaptable. There is even a difference among high-grade spelters, determined by the presence or absence of impurities to the extent of a few hundredths %. Thus, the high-grade spelter of the New Jersey Zinc Co. commands a premium over electrolytic spelter.

Zinc dust is the "blue powder" of the metallurgist. It may be collected as a by-product, or it may be made deliberately by condensing zinc vapor in that way instead of as spelter. Zinc dust may also be made by atomizing molten spelter.

In the United States the principal uses of spelter are for galvanizing, brass making, and for rolling sheet zinc. These uses account for about 90% of the total. The remaining 10% is

employed for the manufacture of French oxide, lithopone, atomized zinc dust, die castings, slush castings, and for the desilverization of lead. Of the use for galvanizing about 50% is for the coating of sheets; the rest for tubes, wire, wire cloth, and shapes (such as buckets, chains, pole-line hardware, etc.). No such detailed information is available in respect to any other country but the European uses are probably analogous to American, except that larger proportions are there employed for sheet zinc and for the manufacture of French oxide (by the combustion of spelter).

Zinc dust is used as a deoxidizing agent in the dyeing industry; as a precipitant of gold from cyanide solution; as a lubricant for pipe joining; and as a pigment (in substitution for red lead) for the protection of iron and steel. The last use appears to be increasing.

An important development in the use of zinc during the last few years has been the increased employment of high-grade spelter for brass making. In the United States about 50% of all the brass in 1925 was made with this grade of spelter, which has practically expelled common spelter from the better grade of brass making. There has been a similar trend of preference in Europe, although perhaps it is not yet so distinctly exhibited over there as it is here.

Economic Conditions.

A year ago it seemed likely that the shortage of supply of zinc ore that had been an important industrial factor for several years previous was likely to continue. There developed, however, a rapid and unexpected increase, the supply to European smelters increasing from about 110,000 tons per month to about 150,000, while at the same time there was an increase in the supply for American metallurgical works.

The reason for this rather dramatic reversal of form was twofold. For one thing the high level of price prevailing for spelter drew out new ore supplies from remote and difficult places, such as Mexico and Bolivia. For another thing the wider introduction of the process of minerals separation by selective flotation made possible the beneficiation of ores that previously had not been worked.

As a consequence of these developments the price for spelter fell, and the averages for 1925 will be in the neighborhood of

7.40 cents St. Louis and £34.3 London compared with 7.62 cents and £36.6 in 1925. The decline was tempered, however, by the increased consumption of spelter, the world's average for the first semester of 1926 having been 104,600 tons per month compared with 99,300 tons average for 1925. The value of ore fell proportionately more than that of spelter, it becoming eventually rather a drug on the market, which resulted in a larger margin for the metallurgists, who consequently enjoyed a good year, while the miners did not have a bad one. Among the metallurgical companies the conditions were best for the electrolytic producers, who occupy an impregnable position. Through the increase in their production, the American distillers felt the effects of such competition. The world's production of spelter in 1926 will be about 1,250,000 tons compared with 1,190,000 in 1925.

The over-built condition of the zinc distilleries of the world, particularly in the United States, produces very competitive conditions among such works, which is intensified by the increasing production of electrolytic zinc, for which several new plants are crystallizing in America, Europe and Africa. Consequently the distillers are constrained to effect improvements in their methods, which, anyway, are compulsory owing to the increasing production of ore in the form of flotation concentrates of excessive fineness which they are bound to treat. Among other things this is forcing the more general preparation of ore for distilling by sintering-desulfurization.

Pyro-metallurgy.

The metallurgy of zinc falls under the heads of pyro-metallurgy and electro-metallurgy. The pyro-metallurgy is necessarily of the nature of distillation, for the reduction-temperature of zinc oxide is higher than the boiling point of the metal. Under the head of distillation a distinction may be made between the process of (1) distilling and condensing, which is the ordinary process for making metal; and (2) distilling, oxidizing and fume collecting, which I have generically characterized as "zinc burning," and which is the method for making zinc oxide. Each of these processes is capable of further subdivision. In distilling and condensing the retort may be coal-heated or electrically-heated, the former being external and the latter internal. Electrothermic distillation may be conducted on the principle of gangue scorification, as at Trollhätten, or on the principle of non-scorification,

as is being done experimentally by Fulton. Zinc burning may be used for the production of refined zinc oxide, suitable for pigment, as in the Wetherill process; or for crude oxide as in the Waelz process and by reverberatory-furnace smelting (as at Florence, Colo.).

Similarly has electro-metallurgy its subdivisions. There are (1) the cyclic, sulfate process, which is the one of general practice, (2) the cyclic, chloride process, which was in use at Winnington, in England, but has now been abandoned, and (3) the electrolysis of molten zinc chloride, which is proposed by Ashcroft.

The world's production of spelter is made principally by the old process of distilling in retorts heated by the combustion of coal, to the extent of about 14% by the cyclic sulfate electrolytic process, and to a trifling extent by electrothermic distillation in Scandinavia. The major production of zinc oxide is made by the Wetherill process (directly from ore) and to a less extent by the French process (by the combustion of spelter). I see no reason to expect any early change in these conditions, beyond foreseeing steadily increasing production of electrolytic spelter. I expect that the distillers will pretty nearly hold their own, but they will be forced to make improvements in practice in order to do so. I do not think that electrothermic distilling as practiced at Trollhätten will make much commercial headway, although metallurgically it is a neat and effective process. In expressing this opinion I am taking no account of the new metallurgical thoughts of the day, which at the best will have a long way to go before attaining commercialization.

JULY 1, 1925:

Group	No. of Plants	No. of Retorts	Capac. of Retorts, Cu. Ft.	No. of Retorts in Use	Per Cent of Retorts in Use	Per Cent of Cubic Feet in Use
East	12	72,522	116,876	49,298	67.98	67.81
West	11	46,384	78,645	35,336	76.18	71.07
Total	23	118,906	195,521	84,634	71.18	69.12

JULY 1, 1926:

East	12	71,908	116,433	45,040	62.64	62.74
West	11	46,344	78,442	35,296	76.16	75.67
Total	23	118,252	194,875	80,336	67.94	67.95

The zinc distilling plants of the United States are grouped as Eastern and Western, the former being arbitrarily defined as those which are east of the Mississippi River, and the latter west. All of the Western plants smelt with natural gas. Of the Eastern plants two use natural gas and the others use coal.

The scale of operation of these plants as of July 1, 1926, compared with July 1, 1925, is shown in the accompanying table.

The decline in the use of retort volume to the extent of only 1.17%, while in retort number it was 3.24%, reflects elimination of the less efficient units. In respect to this subject, however, density of charging and other metallurgical factors play such important parts that further statistical analysis would be futile.

The retorts used by American zinc distillers range in internal length from 48½ to 54½ inches; in diameter from 7½ to 8⅞ inches; in volume from 1.4 to 1.9 cu. ft.

The density of charging of roasted Joplin ore ranges from 27 to 55 lb. per cubic foot, the general practice being 45 to 50 lb. The proportion of furnace capacity used for redistilling between-products (commonly called blue powder) ranges from 15% to 40%, with 20% to 25% the usual thing.

These data exemplify the wide variations in American practice in distilling the same kind of ore in the same kind of furnace.

However, not even should the extremes be criticized without taking into account the cost of smelting and percentage of zinc extraction, there being a correlation among all factors which has a final expression in terms of cost and yield.

In European zinc distilling practice there is even more variation than in American practice, not only as to dimensions of retorts but also as to types of furnace, both for roasting and for distilling.

In the main, however, zinc distilling practice both in Europe and in America remains essentially unchanged as compared with a decade ago. This is not to charge zinc metallurgists with backwardness in thought. They are the victims of physical conditions that constrain them to reduce and distill zinc in relatively small retorts. I do not look, therefore, for any radical improvements in this branch of the practice, but subordinate improvements are being made steadily. These take such forms as the better regulation of furnace temperature, the curtailment of reducing coal, the increase of density of charge, the instruction and improvement of furnace labor, etc.

While nothing radical is to be expected in distilling practice, blende roasting, which is the necessary preliminary, is about to be revolutionized through the installation of what will be described as double-roasting, which means preroasting on hearths down to about 8.5% sulfur and finishing by sinter-roasting on Dwight-Lloyd machines. This practice is being introduced, both in Europe and in America, with several modifications. In its acme, which has not yet been aimed at but will be, the entire process of blende roasting will be performed mechanically, with material labor saving; it will be done autogenously to all intents and purposes, the requirement for carbonaceous fuel being but trifling; a better desulfurization will be accomplished and the ore will be better prepared physically, which will give increased extraction upon distilling; the collection of dust by Cottrell precipitation, which will be necessary, will reduce loss in roasting. This practice constitutes a major improvement in the metallurgy of zinc and its adoption, which is already considerable, is bound to expand rapidly.

Another relatively recent, major improvement in the pyro-metallurgy of zinc has been the burning of a bricketed charge on a mechanicalized Wetherill grate, which was invented by the New Jersey Zinc Co. and has been put into general practice at its works at Palmerton, Pa., for the production of zinc oxide. A mechanicalized Wetherill furnace had long been visualized but was never practicable for the handling of ordinary loose charge. The bricketed charge made it possible. The behavior of the two kinds

of charge is quite different. The loose charge always had to be burned in a sealed furnace, while the bricketed charge is burned with open doors. The new practice of the New Jersey Zinc Co. greatly increased zinc extraction and reduced operating cost, which was not all clear gain, however, for the plant cost is very high.

Electro-Metallurgy.

Of course the major thing of this century in the metallurgy of zinc has been the successful introduction of the cyclic sulfate process of electrolytic extraction, beginning in 1915. Besides the three great plants at Great Falls, Trail, and Risdon, there were in 1925 three small plants in operation, and altogether they made 14% of the world's production. Four new plants are now in course of construction or are definitely planned.

In the 10 years of its practice the electrolytic process has settled down to a matter of routine, and no longer are spectacular innovations to be expected in it. The practice has now been regularized so that a high degree of current efficiency, 90% and upward, is realized right along. Proper purification of electrolyte is the controlling factor. Zinc electro-metallurgists are now agreed that the best deposition of zinc would occur from a chemically pure solution of zinc sulfate. Even the presence of a little manganese is viewed as something that may be tolerated rather than desired insofar as zinc deposition is concerned. The reduction of cost of electrolytic zinc extraction has been largely a function of increase of scale of operations. This is a reason why electrolytic plants are advisably built on a very large scale. In a distilling plant the furnace is the unit, and by increasing the number of furnaces we do not reduce our cost enormously, while in the electrolytic plant it is the department that is the unit.

I do not mean to say that the electrolytic process has now been so thoroughly explored that no new problems will occur. On the contrary, every new ore may present its own problems. Thus, the Rhodesia Broken Hill Development Co. is about to begin treatment of an ore that contains vanadium and soluble silica, both of which must be eliminated in the process. It so happens that the vanadium will be a highly valuable by-product. This ore being a calamine, sulfuric acid has to be added to the process, whereas in the treatment of sulfide ores it is necessary to get rid of acid. Another new problem occurs in respect to the ore

from Reocin, Spain, which is to be treated in Norway. That ore contains a considerable percentage of magnesia that passes into solution and accumulates in the electrolyte, presenting a new difficulty that must be obviated in one way or another.

The Sullivan Mining Co., at Kellogg, Idaho, is to be the first user of the Tainton process of the electrolyzing at high density, 100 amperes per square foot of cathode against 25-30 amperes in ordinary practice. This will reduce cost of plant and is expected to offer other advantages. Mr. Tainton has recently reported improvement in composition of lead anodes, which obviates their deterioration, prevents contamination of the cathode deposits by lead swimming in the electrolyte, and gives a high grade of manganese dioxide at the anode (if the ore be manganiferous).

New Processes.

Numerous new processes having to do with the metallurgy of zinc are now being tested. Charles H. Fulton is experimenting with his method of electro-thermic distilling, which consists in passing electric current through a column of bricketed charge, acting as resistor. This is sound in theory and thought but awaits adequate mechanicalization and commercialization. The National Smelting Co. in Great Britain is about to make a test of the Ashcroft process of electrolyzing molten zinc chloride, which will be wholly a novelty in the metallurgy of zinc, although the idea was first proposed by Ashcroft many years ago. The Roitzheim-Remy distilling furnace, comprising vertical retorts, which is in use at a plant in Germany, especially for the treatment of zinc ashes (a galvanizing by-product), has been examined by American metallurgists, but it is found very costly to build and to offer no operating advantage under American conditions. The Waelz process of burning zinc out of low grade ore in a revolving cylinder, like a cement kiln, is finding some application in Europe, particularly in Upper Silesia, and is likely to extend in use as a helpful adjunct to some existing practices. The American Zinc, Lead and Smelting Co. at its Rose Lake plant is carrying the densification of its retort charge to the degree of overcharging, thus deliberately overtaxing the condensers, the fume that fails to condense being conveyed to bag filtration. Increase of furnace capacity and increase of ultimate zinc extraction are thus both realized, advantageously, according to the

company. The same company is roasting blende at Columbus, Ohio, in the Webb-Wedge furnace without the use of any extraneous fuel, desulfurizing to about 2.5%.

Problems Awaiting Research.

I think that the major problems that we have in the pyro-metallurgy of zinc are of engineering character rather than inventional. In many important respects we know what we ought to do, but are obstructed by the high cost of making the necessary changes in plant. Thus, in American practice we experience a loss of about 3% of our zinc between its entry into the works and delivery to the distilling department, which loss is wholly mechanical and capable of correction by suitable methods. In distilling our greatest loss is in the residue drawn out of the retorts. For a large part of that loss the unevenness of temperature in our furnaces is responsible but we are reluctant to demolish them and substitute more efficient ones. In both of these respects European practice is, on the whole, ahead of American.

The matter of temperature control is highly important in zinc distilling, but the application of pyrometry to that practice has not been satisfactorily developed. Speaking generally we should like to do it, but do not know how. We wish that we could get cleaner coal for our reducing material, but do not know how. A study of the clay retorts that we use, with a view to their improvement, would be most desirable. Similarly as to the clay that is used for condensers, which at present are subject to excessive breakage and carry away a very uncomfortable percentage of our zinc by absorption. It is true that we regain a large proportion of that zinc, but that is done at the cost of mechanical concentration and redistillation.

The charging and discharging of our retorts by mechanical means is a subject that is ever under consideration. This is also an engineering problem rather than one of research. I do not expect that zinc distilling and condensing is ever going to be put on the basis of copper smelting and lead smelting as a continuous operation performed in large furnaces, for the reversibility of the reaction $ZnO + CO = Zn + CO_2$ imposes physical limitations that are severe. We should make a great stride in our existing pyro-metallurgy, however, if we were able mechanically to charge our retorts, putting into each one the same quantity of material and reducing the time of charging; if we could heat

all of the retorts to the same temperature at the same time and regulate the furnace thermograph by pyrometric observation; if we could have more uniform and more durable retorts; if we could have more durable and less absorptive condensers; and if we could proportion the condensing capacity just right. Such improvements, coupled with what may be done in roasting, would greatly increase the percentage of zinc extraction, while reducing cost per ton of ore. The old art of zinc distilling and condensing is far from being exhausted.

The use of zinc presents a great field for research, which would fall under the heads of (1) adapting it better to existing uses and (2) applying it to new uses. Under the former head we have been heretofore rather limited to common spelter which is really a zinc alloy, with its cadmium and lead contents playing important rôles, but under scarcely any control. With the new supply of high-grade spelter it is easy to add to it whatever proportion of cadmium, lead, or other metal may be desired; and there will be an increasing tendency among users of this metal to study and prescribe just the composition that is best for their purposes. Under the second head there are undoubtedly many new uses to which zinc might be applied if more attention were directed to its properties and advantages.

In the pigment field the zinc paints—oxide, lead-zinc, and lithopone—make steady headway, which is a consequence of the upward trend in the price for lead, a metal that is being more and more pre-empted for other, indispensable uses.

Cadmium.

The metallurgy of cadmium is very similar to that of zinc. This sister metal is more easily volatile and is electro-negative, wherefore in the pyro-metallurgical process separation is made by fractional distillation, while in the electro-metallurgical process cadmium is precipitated by zinc from the solution.

In the pyro-metallurgical process cadmium is partly volatilized during the roasting of the ore. That which escapes volatilization in that way and enters into the retorts is there volatilized during the early periods of distillation, wherefore the spelter as condensed and obtained as the "first draw" is higher in cadmium than what follows. Similarly as to the first blue powder. If that blue powder be kept apart and redistilled an enrichment of cadmium is effected, and eventually the isolation of cadmium

may be carried to the point of getting commercially pure cadmium. The concluding redistillation may be done in iron retorts for no very high temperature is required.

Cadmium-containing flue dust and similar between-products may be worked for cadmium in the same way. Or they may be treated hydro-metallurgically for eventual recovery as a chemical precipitate, such as cadmium yellow. Previous to the advent of the process of electrolytic zinc extraction all of the cadmium of the world used to be obtained in the above ways.

In the electrolytic process of zinc extraction it is necessary to eliminate cadmium before proceeding to zinc deposition. The cadmium of the ore goes into solution along with the zinc. From the solution cadmium is precipitated by adding metallic (atomized) zinc. This throws down copper and other metallic impurities at the same time and gives a copper-cadmium-zinc precipitate. From such a precipitate cadmium is redissolved and is retreated for the eventual production of a pure solution of cadmium sulfate, which is then electrolyzed.

The bulk of the world's cadmium is now produced as such a by-product by the electrolytic zinc works, whose scale of operation is so great that the cadmium supply has been largely augmented with a consequently drastic lowering of price.

Unfortunately cadmium is a metal for which there are no widespread uses, not even at the present price. Cadmium electroplating, analogous to zinc electroplating, has been the most important new use. A zinc-cadmium solder is also being introduced. At a much lower price than that which now prevails (60c. per lb.) cadmium would probably come into increased demand for cadmium yellow, a well-known pigment.

Chapter XI.

Heavy Acids.

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There has been considerable advance in the methods of manufacture of the heavy acids during the period covered by this report. In the sulfuric acid industry a marked increase in the use of the contact process has taken place. The installation at the Mond Nickel Company, Coniston, Ontario, where 4½-5½% SO_2 gas from the Bessemer converters is being utilized for manufacture of sulfuric acid by the contact process, is unique in the industry. The capacity of this plant is about 25,000 tons of acid per year, although the available gas would supply a much larger plant. In a number of plants where platinized magnesium sulfate has been employed for some years as the contact mass, platinized asbestos has been substituted. The use of kieselguhr pellets for platinum carriers has found some favor and it is reported that one contact plant is employing a vanadium oxide catalyst.

In some of the Grillo-Schroeder type of contact plants, heat interchangers have been installed in order to eliminate the cost of preheating the gases. Attention has been given to modified types of converters which have for their purpose a better control of the temperature of the gases and of the contact mass. One proposal makes use of a combined converter and heat interchanger. A new converter described by C. R. Downs [1] consists of a shell containing a number of tubes, in which tubes the catalyst is placed and the conversion effected. Temperature regulation is attained by filling the shell with molten sulfur, the temperature of which can be varied by changing the pressure upon it. Changes have been made in the method of purification

[1] U. S. P. 1,547,167; July 28, 1925.

of the gases, so that iron and steel apparatus have largely replaced lead in certain installations.

In the absorption of sulfur trioxide Henry Howard [2] has devised an apparatus consisting of a cast iron bowl so arranged as to circulate acid through a perforated plate in countercurrent to the entering sulfur trioxide gas. Acid is continuously fed into the bowl and 98% acid of practically uniform strength is continuously removed.

In the manufacture of sulfuric acid by the chamber process the most notable step has been the installation of two large Mills-Packard water cooled sets by the Armour Fertilizer Co. at Jacksonville, Fla., and Wilmington, N. C. These sets are operating on somewhat less than 4.75 cu. ft. of chamber space per pound of sulfur with a niter consumption of 3-3½%. These installations are the first to operate in the United States, although they have found considerable favor in England and on the Continent. Several small Mills-Packard chambers are now being erected at Baltimore to operate in conjunction with rectangular chambers. It is interesting to note that in a Mills-Packard system being constructed in England, the chambers will have a capacity of 36,000 cu. ft. each. These chambers are approximately twice the size of any previous installation of Mills-Packard units.

One of the most important changes in the chamber process has been the adoption by several of the large chemical manufacturing companies of the ammonia oxidation process in place of the older methods for introducing niter. The decrease in the price of ammonia has made this commodity more economical than nitrate of soda. It is claimed that a saving is also effected in labor and maintenance by the installation of the ammonia oxidation apparatus, and since the ammonia process is continuous, the chamber process runs more smoothly with ammonia than with nitrate of soda.

J. V. Skoglund [3] claims to reduce the niter losses in the chamber plant by passing the gases from the last chamber through a preliminary Gay-Lussac tower, then through a small scrubbing tower in which they are treated with water or dilute acid solution to decompose the nitrogen peroxide, and finally through the main Gay-Lussac tower where the nitrogen trioxide is absorbed.

[2] U. S. P. 1,565,366; Dec. 15, 1925.
[3] U. S. P. 1,559,292; Oct. 27, 1925.

Henry Howard [4] has found that by cooling burner gases in a dry cooler and then moistening them to the proper degree before filtering, he can reduce the amount of drying acid to about ⅓ of that required in a wet cooling apparatus, and at the same time avoid premature formation of sulfuric acid of corrosive strength in the filters, with consequent damage to the cast iron apparatus.

In the manufacture of nitric acid, the outstanding development is the installation of the ammonia oxidation process in a large way. In the opinion of several authorities this method will, in the near future, supersede the nitrate of soda methods for the manufacture of this commodity. It is interesting to note that, if this prediction is verified, the supply of niter cake and, to a certain extent, salt cake will be seriously curtailed.

In the continuous concentration of nitric acid by the tower system, F. C. Zeisberg [5] has found that if the acid is introduced into the top of the tower at a temperature just below its boiling point, it is more efficiently concentrated. The heating is done by a heat interchanger, and the steam required is blown in near the bottom of the tower. C. W. Cuno [6] bubbles air or oxygen through the heated mixture of nitrate and sulfuric acid in the manufacture of nitric acid, to prevent the formation of nitrogen peroxide fumes.

In the hydrochloric acid industry, direct synthetic methods, using by-product chlorine and hydrogen from electrolytic plants, are being increasingly used in certain localities. Wm. Hirschkind [7] has described an interesting method for making hydrochloric acid from chlorine which is being used commercially on the Pacific coast. A brick-lined furnace is charged with coke, and the coke heated by an air blast to a bright red heat. The air is then turned off and chlorine and steam passed in; the reaction begins immediately and maintains itself. The exit gas from the tower contains from 65% to 70% of hydrogen chloride, which is absorbed in the usual way. The reaction is carried out at between 900° and 1000° and appears to proceed according to the equation

$$C + 2H_2O + 2Cl_2 = 4HCl + CO_2.$$

[4] U. S. P. 1,545,142; July 7, 1925.
[5] U. S. P. 1,546,910; July 21, 1925.
[6] U. S. P. 1,552,117; Sept. 1, 1925.
[7] Ind. Eng. Chem., 17: 1071; 1925.

Hugh A. Galt [8] produces hydrochloric acid of 18° Bé by treating calcium chloride with strong sulfuric acid. The calcium sulfate formed as a by-product is also commercially available. Erwin Schmidt [9] removes arsenic from muriatic acid by treating it with activated charcoal.

Bezanson and Maxim [10] have devised a ceramic furnace for the manufacture of hydrochloric acid. All parts of this furnace which are exposed to the reaction, except the stirrer, are of ceramic materials. Furnaces of this design have been in commercial operation for several years, and the inventors claim a lower first cost, a longer life and lower repair charges for this furnace than for any other type previously employed.

[8] U. S. P. 1,581,436; Apr. 20, 1926.
[9] U. S. P. 1,571 648; Feb. 2, 1926.
[10] U. S. P. 1,544,798; July 7, 1925.

Chapter XII.

Salts and Non-Metallic Inorganic Substances.

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This review of American advances, research tendencies and needs in the field of salts and non-metallic inorganic substances for the current year, can have neither time nor space to go deeply into detail. Emphasis will be thrown mainly, therefore, upon a few far-reaching tendencies—at the risk of the omission of what may be really important matters to some.

In the industrial field applications rarely come into use with a jump. Even an outstanding new departure, while perhaps final for a given investment, is nevertheless merely on trial before the industry as a whole. Substantial progress comes as a development, therefore, over a period of time. Individual opinion obviously would greatly vary as to the real accomplishment at any stage of a new proposal or development.

I. Recent Advances in the Study of Salts and Non-Metallic Substances.

In studying the salts of the rare elements, the outstanding development of the year is the fact that Professor B. S. Hopkins,[1] of the University of Illinois, feels that he has clinched the discovery of element number 61. He has called it Ilinium, with the symbol Il, after the old Illinois Indians, State of Illinois, or its University. Dr. Kiess of the United States Bureau of Standards found some time ago 130 lines common to the spectrum of both neodymium and samarium, presumed to be pure, but which checked with none of the lines of any known element. Acting on the suggestion that these lines might be due to the presence of the undiscovered element number 61, work under the direc-

[1] Harris and Hopkins, J. Am. Chem. Soc., 48: 1585; 1926. Harris, Yntema, and Hopkins, J. Am. Chem. Soc., 48: 1594; 1926.

tion of B. S. Hopkins was commenced in an effort to isolate this element. L. F. Yntema, coöperating with Professor Hopkins, studied fractionations with X-ray methods at Yale University, yielding no direct evidence. The arc spectrum gave 5 new lines in the ultra-violet from intermediate fractions. This led to the conclusion that if element number 61 were present it must be to an extent less than one per thousand. G. A. Harris, coöperating with Hopkins, studied fractional crystallization with double magnesium nitrates and bromates, finding a new line in the absorption spectrum of the intermediate fractions, eventually leading to heavy absorption bands which could only be due to a new element. These fractions subjected to X-ray examination developed the theoretical lines for number 61. The discovery of the new element is based upon evidence supplied by the diminution of lines in the fractions containing known elements, and the increase of lines in intermediate fractions, using arc spectra, absorption spectra and X-ray spectra.

The salts of the element hafnium are being studied. Hevesy and Kimura [1a] have determined the solubilities of zirconium and hafnium phosphates in 6*N* hydrochloric acid and have found that the solubility of zirconium phosphate amounts to 0.00012 molecular equivalents and that of hafnium phosphate 0.00009 molecular equivalents. In 10*N* acid the values are 0.00023 and 0.00012.

Years of work on selenates by Lenher has added much to our knowledge. Lenher and Kao [2] have now prepared from the mixed acid obtained by the direct chlorination of selenious acid a number of selenates by neutralization with the carbonate of the metal. By the use of the carbonates of lead, barium, calcium and strontium the selenates are obtained as precipitates. Selenates of copper, cadmium, cobalt, nickel and magnesium are separated from the chlorides by dissolving the latter in acetone or alcohol. They have also studied the preparation of selenium monochloride and monobromide. They studied the properties of the monochloride.[3]

Victor Lenher and Eugene J. Wechter [4] have contributed to our knowledge of selenic acid and the selenates.

C. W. Muehlberger and Lenher [5] have studied the addition products of selenium dioxide with the halogen acids. Studies

[1a] J. Am. Chem. Soc., 47: 2540; 1925.
[2] J. Am. Chem. Soc., 47: 1521; 1925.
[3] J. Am. Chem. Soc., 48: 1550; 1926.
[4] J. Am. Chem. Soc., 47: 1522; 1925.
[5] J. Am. Chem. Soc., 47: 1842; 1925.

on the chemistry of gold are of value in certain phases of geological theory. Lenher and Kao [6] have gone into the study of the partition coefficients of gold salts. Thallium still continues to furnish interesting salts. Lindsley and Dennis [7] have described the following new compounds: $Tl_2SeO_4 . CuSeO_4 . 6H_2O$; $Tl_2SeO_4 . CoSeO_4 . 6H_2O$; $Tl_2SeO_4 . NiSeO_4 . 6H_2O$; $Tl_2SeO_4 . MgSeO_4 . 6H_2O$ and $Tl_2SeO_4 . MnSeO_4 . 6H_2O$.

The study of oxides of nitrogen has long aroused interest. Now we need all the knowledge of these bodies we can secure. Hasche [8] has identified and prepared a compound having the formula $(N_3O_4)_x$. This compound was prepared by the interaction of nitric oxide and oxygen at liquid air temperatures. Hasche and Patrick [9] have found from their investigations that the velocity of the reaction between nitric oxide and oxygen at 30° is of the third order; that a large increase in the surface to volume ratio by the introduction of glass wool into the reaction chamber caused a marked acceleration in the velocity constant in the latter half of the experiment; that no evidence of autocatalysis was obtained; that the negative temperature coefficient has been ascribed to intermediate compound formation.

Fluorine compounds deserve more study. Tosterud [10] has prepared hydrated aluminum fluoride of the composition $Al_2F_6 . 18H_2O$ from aluminum hydrate and aqueous hydrofluoric acid. He has also prepared the anhydrous fluoride by subjecting the above crystalline compound to high temperature.

Silica gel has proven its value in scientific work and is still struggling industrially. Holmes and Anderson [11] have developed a new type of silica gel. The gel is made by the addition of dilute ferric chloride solution to a dilute sodium silicate solution. The gel is first dried rigid before washing to prevent the collapse of the capillary walls. The ferric oxide can be removed by soaking in dilute hydrochloric acid, washing and drying. The coarser capillaries are said to make it a better decolorizer and more absorbent.

The absorptive capacity of substances such as alumina has resulted in interesting chemical developments. Munro and Johnson [12] have studied the adsorption of vapors by alumina. It was

[6] J. Phys. Chem., 30: 126; 1926.
[7] J. Am. Chem. Soc., 47: 377; 1925.
[8] J. Am. Chem. Soc., 47: 2143; 1925.
[9] J. Am. Chem. Soc., 47: 1207; 1925.
[10] J. Am. Chem. Soc., 48: 1; 1926.
[11] Ind. Eng. Chem., 17: 280; 1925.
[12] Ind. Eng. Chem., 17: 88; 1925.

found to be a good adsorbent for such vapors as gasoline, ether, alcohols, sulfur dioxide and ammonia, all of which can be recovered. It is not suitable for the recovery of such vapors as acetone, ethyl acetate, amyl acetate, alkyl halides and acetyl chloride and bromide. For some, such as acetone, decomposition catalysis accompanies adsorption and they cannot be recovered from the alumina. The adsorption power depends on the state of hydration, the greater the hydration the greater the adsorption. The alumina is prepared by heating pure hydroxide in the form of a fine powder in a U tube for 2 hours at 400° C. in a bath of potassium and sodium nitrates, while at the same time passing dry air through the alumina.

Maier [13] has studied the vapor pressure of the common metallic chlorides and a static method for high temperature vapor pressure measurements. The vapor pressures of the common metallic chlorides were determined over a range up to 1250° C. The containers were of pyrex up to 600° and above that of clear fused silica. An electric tube furnace was used for temperatures of 300° to 1300°, and an oil bath up to 300°. The method gave results which were considered satisfactory for engineering purposes. The data are collected in the form of graphs and tables.

The control of the color and other factors in antimony sulfide manufacture has always been of interest. Currie [14] has reached the following conclusions concerning antimony sulfides: That precipitated antimony sulfides are all amorphous solids; that all antimony sulfides can be converted into the black crystalline modification of the trisulfide; that the amorphous trisulfide in a fine state of subdivision is yellow; that there are maroon shades of antimony trisulfide; that a crystalline yellow antimony trisulfide may be prepared; that crystalline crimson pigments cannot be prepared by the methods studied.

Besides theoretical importance the value of knowledge of salt behavior in anhydrous liquids is at times vital in utilization. Davidson [15] has made the following statements in regard to the solubility of salts in 100% sulfuric acid. Salts of metals whose sulfates are insoluble in sulfuric acid are insoluble; salts of free acids which, in the free state, are insoluble in sulfuric acid are insoluble; salts of metals whose sulfates are soluble and of acids which are soluble, are, in general, soluble in 100% sulfuric acid;

[13] U. S. Bureau Mines, Tech. Paper, No. 360.
[14] J. Phys. Chem., 30: 205; 1926.
[15] J. Am. Chem. Soc., 47: 968; 1925.

double decomposition reactions take place readily between ionized salts in sulfuric acid.

Iron oxide pigments are such common materials that they have been almost forgotten by investigators. American ochers are well known to give irregular satisfaction. Rhodes and Cooper [16] have studied the effect of yellow and brown iron oxide pigments upon the rate of oxidation of linseed oil. Ochers tend first to retard and then to accelerate the drying of the oil. The initial retarding is caused by the adsorption of the drier from the oil. The final acceleration is due to the formation of iron soaps which act as catalysts. The iron oxide in an ocher reacts less readily with a drying oil than does ferric oxide in a red iron oxide pigment. Siennas and umbers show less retardation on the initial rate of oxidation of the oil than does ocher, because the removal of the lead drier is compensated by the formation of a small amount of manganese drier.

The scientific study of photography actively continues. Trivelli and Sheppard [17] have investigated the visible decomposition of silver halide grains by light and have reached the following conclusions: That photochemical darkening of specially prepared silver bromide occurs in definitely oriented patterns depending upon the growth and structure of the crystal; that the visible darkening of silver bromide emulsions, which were studied statistically, is irregular, and the visible sensitivity of different emulsions is due to the fact that the visible sensitivity is relatively independent of sensitivity nuclei; that photochemical decomposition is oriented in the crystal according to the gradients of ionic deformation, or perturbation of electron orbits following certain directions of growth.

In studying the catalytic influence of silver salts, Yost [18] has determined the rate of reaction between peroxysulfuric acid and chromous sulfate when catalyzed by silver salts at the temperatures 25° and 35° and found that it is proportional to the first power of the concentration of peroxysulfate ion and of the silver ion, but to be independent of the concentration of the chromic ion. These facts indicate that the silver ion acts as a carrier catalyst through the formation of a trivalent silver salt as the intermediate compound, and that the reaction takes place in two steps.

[16] Ind. Eng. Chem., 17: 1255; 1925.
[17] J. Phys. Chem., 29: 1568; 1925.
[18] J. Am. Chem. Soc., 48: 152; 1926.

The action of ultra light on salts was studied by Getman [19] who has investigated the absorption of ultra-violet light by inorganic halides. His results may be summarized as follows: That the chlorides of calcium, magnesium, zinc and aluminum have been found to absorb ultra-violet radiation selectively, the wave length corresponding to the head of the absorption band of each salt being approximately 273 μμ; that the persistence of this characteristic absorption through a series of chlorides cannot be attributed to the presence of the common ion chlorine; that solutions of calcium chloride do not follow Beer's law; that the molecular extinction coefficients of the metallic chlorides increase with the atomic weight of the combined metal; that while certain metallic chlorides do not exert selective absorption, they, nevertheless, exert marked general absorption.

It is quite common to attribute to a single component of unusual individuality the properties of the equilibrium or system. Vincent [20] has reached the following conclusions, however, for the use of potassium bichromate as a depolarizer: That a saturated solution of the bichromate has practically no depolarizing action on hydrogen set free at a smooth platinum cathode; that a saturated solution of the bichromate shows 100% depolarization for hydrogen set free at a clean mercury cathode; that the addition of about 0.7 cc. of concentrated sulfuric acid to 250 cc. of saturated bichromate solution is necessary before there is appreciable depolarization of hydrogen at a smooth platinum cathode; that zinc, iron and copper do not corrode appreciably in a saturated solution of the bichromate; that copper does not corrode appreciably when short-circuited with platinum in a saturated solution of the bichromate; that copper and iron do not corrode appreciably when short-circuited with mercury in a saturated solution of the bichromate; that different amounts of concentrated sulfuric acid must be added to a saturated solution of the bichromate in order to cause zinc, iron and copper to corrode.

Adding to our list of accurately known solubilities is always worth while. Archibald and Hallett [21] have determined the solubilities of the chloroplatinates of rubidium and cesium in water at temperatures between 0° and 100° at 10° intervals. Crew,

[19] J. Phys. Chem., 29: 853; 1925.
[20] J. Phys. Chem., 29: 875; 1925.
[21] J. Am. Chem. Soc., 47: 1314; 1925.

Steinert and Hopkins [22] have worked out in great detail the solubilities of yttrium nitrate, chloride, bromide and sulfate. The results expressed in parts per 100 grams of water indicate a solubility for the nitrate of 93.1 at 0° and 211 at 66.5° C.; for the chloride 74.3 at 0° and 78.1 at 80° C.; for the bromide 61.81 at 0° and 131.33 at 95° C.; for the sulfate 8.016 at 3° to 6° and 2.007 at 95° C. Williams, Fogg and James [23] have determined the solubilities of hexahydrated trichlorides of yttrium, samarium, and neodymium in water and hydrochloric acid of a density of 1.1051, and of yttrium in the latter solvent at intervals of 10° from 0° to 50° C.

It was considered that a careful study of the solutions of the chlorides might reveal some striking characteristics available for the separation of certain members of the rare earth series.

The chemistry of non-aqueous solvents is always suggestive and often of considerable value. Bergstrom [23a] has called attention to the fact, which had already been pointed out by Franklin and Kraus,[24] that ammonium salts behave as acids in liquid ammonia solution. It has been shown in conjunction with earlier work, that solutions of ammonium salts react with most of the elements above hydrogen in the electro potential series.

It is understood in the industry that the secret has been discovered of preparing hypochlorites of a purity and stability hitherto unknown, *i. e.* $Ca(ClO)_2$ with a loss of strength of 0.5% in six months.

Great electrical insulating power has been developed by mixing ground mica in fusion with lead borate. The product is expected to displace the more cumbersomely manufactured porcelain.

Window glass manufacturers are keenly watching for possible displacement of glass for greenhouses by organic chemical developments.

II. New Uses of Compounds.

The effort to find outlets for expanded chemical engineering facilities in the wake of the war still continues. An effort is now being made to manufacture benzoic acid from toluene by its direct oxidation by nitric acid at Nitro, West Virginia.

[22] J. Phys. Chem., 29: 34; 1925.
[23] J. Am. Chem. Soc., 47: 297; 1925.
[23a] J. Phys. Chem., 29: 160; 1925.
[24] Am. Chem. J., 23: 305; 1900.

Coblens and Bernstein [25] have found that one drop of ferrous sulfate solution in a stannous chloride solution causes the evolution of nitric oxide when nitric acid is added; that titanous chloride reduced nitric and nitrous oxide to ammonia; that nitric oxide is evolved and no ammonia is formed when silver hyponitrite is added to an acid titanous chloride solution; that titanous chloride has a specific decomposing effect on nitrous and hyponitrous acids; that hydroxylamine is formed when a silver hyponitrite solution is added slowly to a solution of stannous chloride; that ammonia has been qualitatively shown to be one of the reduction products when nitric acid reacts with sodium hyposulfite.

The value and limitations of sulfides in combating fungi are well known. Lougee and Hopkins [26] have studied selenium compounds as spray materials. Leaf injury of selenium compounds is too great for successful use. Some success is in prospect in the use against pests such as pear blight. The most promising use is for the eradication of such lawn pests as dandelions and plantains.

Crocker [27] has found a remarkable property of selenium. The element selenium is an excellent flame proofing material for insulating wire. Some of its compounds, such as sodium selenite and selenium oxychloride, are good also. The powdered element is best. It is applied with an adhesive to rubber covering of wire under cotton braid or by impregnating the braid.

The campaign by the National Research Council Committee on the replacement of potassium by sodium compounds has been continued throughout the year. A number of additional investigators have been interested in the subject. Physicists have developed the making of mirrors of satisfactory quality without the use of potassium compounds. Many textbook methods used in the teaching of chemistry have been shown to work equally well with sodium compounds, and manufacturers have been encouraged to keep up, where possible, the work of encouraging the use of sodium in place of potassium. Some of this material is nearing publication and some of it, as in the United States Pharmacopœia and in the Methods of the Official Agricultural Chemists, has already been published.

Calcium cyanide is now prepared on a commercial scale and

[25] J. Phys. Chem., 29: 750; 1925.
[26] Ind. Eng. Chem., 17: 456; 1925.
[27] Ind. Eng. Chem., 17: 163; 1925.

sold as "powdered hydrocyanic." It finds a ready use for fumigation of fruit trees. This is an outstanding development.

The demand for bromine has been increased by the fact that it is the only material which gives any promise of relief from the bad effects of lead tetraethyl when used as an anti-knock material in gasoline motors. It appears that the elimination of lead in the form of its bromide offers the only secure method of preventing corrosive action of lead compounds upon the various portions of the combustion chamber.

The air nitrogen industry demands new fertilizer salts more acceptable to the trade. A mixture of ammonium nitrate and ammonium sulfate appears less hygroscopic than either salt alone, as is pointed out by Curtis.[28] Conditioning of concentrated hygroscopic fertilizer materials by "graining," which consists in spraying the molten or highly concentrated salt into air so that the drop hardens and falls in grains with minimum surface exposed, is one of the developments in this material. Urea, calcium nitrate, ammonium nitrate and ammonium phosphate are so treated.

Lime and Trade Wastes. The value of lime in the treatment of trade waste effluents is being strongly emphasized. It has been difficult to impress sanitary engineers with the idea that lime fluctuations in composition and physical properties were vital factors in its availability for a given purpose. Some success along this line is now developing. Besselievre[29] states that for the prevention of stream pollution, chemical treatment is in most cases necessary to produce a water-white, neutral effluent. Lime alone, or a combination with some other chemical, often produces the desired results. Where acidity is to be removed or solids precipitated lime is usually the ideal agent. After the formation of the floc by other agents lime precipitates this floc. Lime may be used to treat wastes from the following industries: laundries; distilleries; textile mills; tanneries; rubber reclaiming plants; coconut products; strawboard mills; paper mills; gun-wadding; roofing paper; banana oil; gas houses; creameries; canneries; packing houses; steel and iron works and sugar factories. Lime sludge is voluminous. Duplicate settling tanks or clarifiers are needed. Chemicals must be thoroughly mixed with the waste. Lime is best fed to the waste in powdered hydrated

[28] Chem. Met. Eng., **33**: 408; 1926.
[29] Chem. Met. Eng., **32**: 634; 1925.

form. Lime stands pre-eminent in possession of practical value and at the same time has the elements of economy, easy procurement, and ease of handling.

III. Advances in Industrial Manufacture of Salts and Non-Metallic Inorganic Substances.

Chlorine is a commodity of great chemical value, and of fluctuating over production. Its chemical utilization, therefore, is the subject of considerable development in the organic field. One of the most tempting lines of this utilization is shown by the statement that over 4,000,000 pounds of ethylene glycol were produced this year from ethylene chlorohydrin as an anti-freezing compound for automobile radiators and at one-half the price of a year or so ago. It is believed that this utilization of chlorine will double in amount in the coming year and that the expensiveness of the synthesis will be cut in two.

Hypochlorites for Bleaching. Bleach makers have long known that water in the lime hydrate was a factor in manufacture. Physical and chemical factors also influence the value of the product. Richardson, Emley and Porter [30] state that the amount of water used in the hydrating of lime for bleaching power should be carefully controlled. The percentage range found to give the best results is from 33½% to 55% water based on the weight of lime used. The most satisfactory product is obtained when 55% water is used. The strength of bleach fell rapidly with increase in percentage of water used. Carter [31] has studied the effect of sodium silicate in counteracting the weakening of fabrics caused by calcium hypochlorite bleaching solution as well as color improvement due partly to silica deposition, and partly to increased whitening of fabric. The most alkaline silicate of commerce is the most effective.

The chemical treatment of refrigeration brines to prevent corrosion is of engineering interest. Poste [32] recommends for making calcium chloride brine a chloride free from magnesium chloride. The gravity of the brine should be kept in the neighborhood of 1.20. Either calcium or sodium chloride brine should be treated with pure quicklime on a basis of 10 pounds lime per 1000 gallons (1.2 kg. per 1000 l.) of brine, or with caustic soda on a basis of 13 pounds per 1000 gallons (1.6 kg. per 1000 l.).

[30] Chem. Met. Eng., 32: 936; 1925.
[31] Ind. Eng. Chem., 18: 248; 1926.
[32] Ind. Eng. Chem., 17: 131; 1925.

The reagents should be added as a slurry or solution at a point of rapid circulation of the brine, though the introduction of caustic in a bag is reasonably effective. Additional reagents should be added from time to time by the foregoing method as may be necessary to maintain the maximum alkalinity for the brine involved. Undue contact between the brine and air should be avoided.

The determining point is the solubility of calcium oxychloride. The limiting factor is the precipitation of the excess of this basic salt. The solubility of the calcium oxychloride increases with temperature and changes but slightly with the gravity of the brine. The conditions of this work eliminate magnesium containing brines but will by no means convince producers of such. White [33] has studied the action of calcium chloride brines on galvanized coatings. He finds that nearly all brands of commercial calcium chloride attack galvanized coatings. The effect of alkalinity is the reverse of that on iron—neutral solutions have much less corrosive action on zinc-coated surfaces. Corrosion is increased by dilution of the brines of high alkalinity. Calcium chloride brines of low alkalinity are much more corrosive when contaminated by ammonia.

Synthetic Ammonia has been making rapid strides in this country since the war. The l'Azote plant at Charleston, West Virginia, is one of the latest plants and is operating advantageously by the Claude process. This is having a profound effect upon the manufacture of pure ammonium compounds, and liquid ammonia, itself. No purification is required of the synthetic product. All such costs and handlings are eliminated. The future of by-product ammonia will be limited undoubtedly to fertilizer uses because of the purification factor. The chemical engineering problems of these ammonia plants are not entirely solved.

Benson [34] describes the making of sodium nitrite by the arc process with hydroelectric power at LaGrande, Washington. The furnace consists of three concentric concrete tubes; the arc being in the inner tubular space, air passes in series through the annular spaces thence through ports, spirally distorting the arc where the reaction occurs. Gases are cooled in a fire tube boiler and pass through 3 towers packed with webbed tile, countercurrently to soda ash solution. Formation of sodium nitrite results. After

[33] Ind. Eng. Chem., 17: 503; 1925.
[34] Chem. Met. Eng., 32: 803; 1925.

nearly complete reaction the liquor is evaporated, crystallized, and the crystals centrifuged. The NO content of the gases is slightly less than 2% by volume. Rigid control of conditions of oxidation and crystallization must be maintained to produce technical sodium nitrite. Secondary reaction produces some nitrite.

$$N_2 + O_2 \longrightarrow 2NO$$
$$4NO + O_2 \longrightarrow 2N_2O_3$$
$$N_2O_3 + H_2O \longrightarrow 2HNO_2$$
$$Na_2CO_3 + 2HNO_2 \longrightarrow 2NaNO_2 + H_2CO_3$$
$$2N_2O_3 + O_2 \longrightarrow 4NO_2 \text{ (secondary reaction)}$$

Almquist, Gaddy and Braham[35] have studied the recovery of nitrogen oxides from gas mixtures by adsorption on silica gel, an important matter in the recovery of nitrogen oxides in the catalytic oxidation of ammonia, fixation of nitrogen by the arc process and nitrogen oxides as by-products. Commercial gels were used in these tests. Adsorption efficiency decreases markedly with rise in temperature, and refrigeration is desirable for adsorbing the oxides. The rate of gas flow has no effect on the final capacity but increased rate lowers the efficiency so that it would affect the quantity of gel to be used. Efficient recovery of dry N_2O_4 can be effected in a short time at 100° C. When water vapor is present the refrigeration of the oxides is more difficult due to the formation of nitric acid. The ratio of nitrogen oxides to water in the recoverable product will depend upon the concentration of each in the gas phase and also on the length of time the gel has been exposed to the gas mixture. If the concentration of water vapor is 1% or less the gel will continue to adsorb water long after it passes practically all the nitrogen oxides.

One of the cleanest cut developments is the making of phosphoric acid in the Southern Appalachians. It gives the keenest pleasure to the chemical mind to see ten car loads of water white 75% phosphoric acid leaving the plant at Anniston, Alabama, each day. The success of this project appears to hinge upon the thorough working of the Cottrell process and the successful use of certain materials for electrodes, about which not much is yet publicly known. The operation is an electric furnacing one. The charge is phosphate rock, quartz sand and carbon. The phosphorous pentoxide is thrown down from the

[35] Ind. Eng. Chem., 17: 599; 1925.

gases by the Cottrell precipitator with atmospheric water, giving phosphoric acid. Rubber-lined tank cars are used for shipping the product.

The hydration of lime is one of those simple chemical operations which proves highly sensitive on a manufacturing scale, yet which probably requires knowledge of but few simple principles to adequately control. Whitman and Davis [36] have studied the effect of excess water, agitation and temperature on the rate of hydration and the grade of product. High-grade hydrate contains many fine particles which are produced when the rate of hydration is rapid; coarse hydrate is produced when the rate of hydration is slow and time given for crystal growth. Excess water, reasonably high temperature and agitation favor the fine hydrate. Excessive high temperatures are detrimental. Evaluation was made by testing the rate of reaction with acid, and the rate of settling in water, also microscopic examination. Using the rate of reaction with acid as an index: 1. The use of excess water produces a finer grained hydrate than the calculated amount of water or vapor. 2. Boiling increases fineness. 3. Increased temperature (not boiled) increased fineness slightly when excess water was used. 4. Vapor hydration was about the same as with calculated water.

Using the rate of settling as an index: 1. Excess water and boiling produce slow settling hydrates. 2. Low temperatures with excess water shorten the settling time. Agitation promotes fine grained hydrate by preventing clustering of the crystals. Higher temperature has a like effect.

Glass. With outstanding developments in the glass industry considered from the standpoint of the inorganic chemical field the transition has been gradual.

Selenium or its salts are in practically universal use at the present time for decolorizing glass. It requires the use of cobalt oxide and gives a color more easily obtained which is also more stable at melting and refining temperatures.

Lead glass is not made in volume as formerly. The demand for heavy cut glass has largely fallen off and as a consequence the amount of lead glass made is small.

Alumina has found wide use as a glass making oxide especially in recent years. It is obtained principally from feldspar, but

[36] Ind. Eng. Chem., 18: 118; 1926.

the manufactured hydrate is used, as well as certain other sources such as lepidolite and china clay.

Magnesia has replaced calcium oxide in many glasses. The Northern Ohio dolomite field is particularly low in iron content which has made these dolomite stones very popular for flint glass and tableware in general.

Salt cake is not as widely used as formerly as an alkaline fluxing agent and source of sodium oxide in glass. This is due to the fact that salt cake was largely used in window glass factories making glass by the "hand" process. The "hand" process has been almost eliminated in the window glass business and the factories using sheet glass machinery obtain most of the required Na_2O from soda ash. Incidentally it might be noted that machine-made window glass will generally require more Na_2O than did hand-made glass. Thirty per cent of the soda ash production now goes to the glass trade.

The plate glass industry has always been very wasteful. It has been found by a study of geometry that a large portion of the waste was in the cutting of the sheet, and that a large portion of this could be eliminated by more scientific methods of cutting.

Sodium sulfate. High-grade sodium sulfate by solar evaporation is proposed from natural sources.[37] A government lease for 20 years has been granted the California-Nevada Sodium Sulphate Co. on 1440 acres of saline deposit near Wabuska, Nev. Typical analysis of crust material runs Na_2SO_4 98.19%, Na_2CO_3 0.13%, NaCl 0.23%, insol. 0.52%, moisture 0.23%, loss at 110° 16%. The method used is to flood the surface of the lake with water, dissolving the salts, which crystallize. This results in about 2 or 3 feet of crude sulfate. The deposit is then reflooded with water to a depth of three inches. The water evaporates and leaves a crop of high-grade crystals. These are removed and the process repeated. The harvested crystals are dried in the sun for 15 days and then crushed. Analysis of crystals runs Na_2SO_4 99.59%; impurities 0.32%; moisture 0.09%. The depth of the deposit is 8 feet. Water supply is derived from wells at a depth of 60 to 80 feet.

Palmer [38] discusses the refining of natural salt cake. Deposits at Soda Lake in the Carrizo Plain shows an analysis of Na_2SO_4 70%, NaCl 14-15%, $MgSO_4$ 7-8%, insol. 2-3%. It is harvested

[37] Chem. Met. Eng., 32: 4; 1925.
[38] Chem. Met. Eng., 32: 632; 1925.

by breaking the surface crust and forking into side dump cars. The cake is crushed to 10 mesh and passed to 3 duplex classifiers in series. Here the salt is washed with a current of cold water, which removes mud and the greater part of the NaCl. The classifier product is agitated with water at a temperature above 90° F. to prevent the formation of Glauber's salt. Here the remaining chloride and the magnesium salts go into solution and also some of the sodium sulfate. The batch is then centrifuged and washed for 40 seconds with hot water. The product runs Na_2SO_4 96%; NaCl 0.5%; $MgSO_4$ 1.5%; insol. 0.4%; water, 1.6%. The plant handles 100 tons crude per day, producing 60 tons of salt, consuming 140 h.p. The product is free from iron and acid, besides being in loose crystals. Kraft paper mills and glass factories are big users. Due to freight rates the eastern boundary is a N-S line through Chicago and New Orleans.

Sources of potash are always of interest. Turrentine, Whittaker and Fox [39] have reported upon greensand (glauconite) as a potash resource in America. There are large deposits of greensand in New Jersey containing about 6.5% K_2O, 6% Al_2O_3, and 18% Fe_2O_3. Greensand is composed of unconsolidated material, the mineral particles are of fairly uniform size (20 mesh), composition and appearance. The green color is due to the presence of glauconite, $KFeSi_2O_6$ aq. The general cause of previous failures to extract potash commercially has been the lack of by-products to help carry the load of manufacturing costs. Several processes gave promise of commercial success. The Tschirner process consists of roasting a mixture of 10 parts greensand, 12 parts lime sand (a calcareous sand found nearby) and 3.5 parts salt to 800° C. The resulting mass is leached and the potassium recovered as KCl by fractional crystallization. The Shreve process consists of the following steps: (a) Fine grinding, 90% through 200 mesh; (b) digestion 1 hr. at 470° to 480° F.; (c) charge 1 part greensand, 0.9 parts CaO, 5 parts water; (d) addition of various salts especially sodium nitrate for the purpose of accelerating the reaction and increasing recovery, and to change the KOH to other potassium compounds. The Moxham process of the Electro Co. has recently been developed. Greensand from the pits is treated with hot dilute sulfuric acid (sp. gr. 1.3 to 1.4). With 50% excess acid at 85° to 90° C. the extraction is complete in 5-6 hours. The in-

[39] Ind. Eng. Chem., 17: 1177; 1925.

soluble residue of granular silicious material is settled or filtered. The clear solution contains sulfates of potassium, aluminum and iron. The mixed sulfates are crystallized out and the mother liquor returned to the process. The mixed sulfates are roasted at 500° C. to decompose the iron sulfate to the oxide. Potassium and aluminum sulfates are leached out and crystallized. The alum is roasted at 900° C. to produce alumina from which the potassium sulfate may be removed by leaching. In each roast the acid is recovered. The products are thus: (a) Iron oxide and ochers; (b) the silicious skeletons of the greensand grains, which are ground and freed from quartz and sold as an absorbent "Glaucosil"; (c) alum and aluminum sulfate; (d) potassium sulfate; (e) fuming and other sulfuric acids. This is a visionary program natural at the early stage of the development.

A number of inorganic chemical industries have been greatly aided by certain chemical engineering developments, directly dependent upon organic chemistry. The most recent of these is probably the rubber-lined tank car. The rubber is now applied integrally in steel tank cars without the intermediation of a hard rubber layer which would be damaged or shattered by impact. The rubber is cemented thoroughly to the steel and vulcanized in place. Great tonnages of hydrochloric acid are shipped about the country in these rubber-lined tank cars. The pickling departments of the iron and steel industries have always found their waste disposal a serious matter. The rubber-lined tank car is serviceable in transporting and disposing of this material at a distance from the plant. The rubber-lined tank cars enable the chlorine industry to lay down hydrochloric acid cheaper to the consumer than has ever been done before. The use of glass carboys is thus entirely eliminated. The shipping of strongly corrosive materials, such as sodium hypochlorite, in a water-white condition in rubber-lined tank cars is greatly appreciated by consumers. The shipment of water white phosphoric acid under the same conditions is a real advancement. In addition to this fact the losses have been reduced to zero. Formerly it was no uncommon thing to experience a loss of as high as $36,000 per year by seepage to accompany the handling of an equivalent to a rubber-lined tank car of phosphoric acid. The whole corrosion question is of great importance in the industry from the point of view of contamination and discolora-

tion. Glass has done much to eliminate this trouble but rubber lining is rapidly improving the situation still further.

W. H. Scott [40] emphasizes the importance of using *dissolved* alum in the beaters. Scores of paper mills have found that it is to their advantage to discontinue the use of dry alum in the beaters and now are introducing the alum as a solution. From the records of many of these mills regarding the cost and amount of alum used before and after installing the alum solution system, the following points in favor of the dissolved alum arise: (1) Labor saving; (2) space saving; (3) improved beater room conditions; (4) elimination of (a) impurities, specks, spots, etc., in the finished product, and (b) more uniform color in tinted stock; (5) improved behavior of the paper in the machine, particularly regarding breakage and smooth passage over the rolls; (6) more perfect precipitation of size in the beaters; (7) saving in alum used. The use of dissolved alum has been made possible by the use of the alloy duriron, which is not attacked by the alum solution.

The use of copper compounds and ammonia in the manufacture of artificial silk has received a new impetus in this country at the great plant at Elizabethtown, Tennessee, where the fundamental success of the process is understood to hinge upon the economic recovery of these materials from the solvent.

The use of sulfuric acid for the pickling of iron and steel, an ancient metallurgical adjunct dependent upon chemical corrosion, is being made much more efficient by the introduction of special corrosion retardants in the shape of aromatic organic chemical compounds which seem to inhibit the action on pure iron while interfering but little with the corrosive action on the oxide.

The developments in the Belgian Congo continue to have a profound effect upon certain American manufacture. Everything connected with American radium has ceased operating and American companies have become distributors, at least until this high-grade African ore shall have changed in quality or have diminished in quantity. Vanadium recovery, however, is again under way in Colorado.

IV. Researches Under Way to Improve Manufacturing Processes.

The increase in kraft paper manufacture by the sulfate process creates quite a demand for cheaper sodium sulfate. The investi-

[40] The Paper Mill, 49, No. 7: 4; 1925.

gations on this are intensified at present. Other factors enter, however, for the decreasing use of sulfate glass batches in the mechanical window glass process will greatly reduce the demand for salt cake in the glass industry.

The value of clay in many refining processes connected with oils and organic substances has been increasingly recognized in recent years. Investigations of deposits from widely different sources in all parts of the country are quietly but persistently being carried out. It is interesting to note, however, that increased engineering efficiency in the recovery of these clays is believed by petroleum refiners to cut in two the cost of refining lubricating oil and has almost made them cease the purchase of clay. This will probably not always hold true, but doubtless the same type of engineering efficiency will be of great value in the vegetable and other oil industries as far as reclaiming clay is concerned. It is surprising to find how extensive is the discard of such materials after one usage, presumably on the ground of original low cost, and probably also because of the tendency to fire hazard on storage preliminary to reburning.

The development of utilization of our clay deposits in every field will reach unbelievable proportions in the next decade.

The new contacting processes for the use of clay in the refining of lubricating oil, in which the clay is brought into intimate contact with the oil and then filter pressed, are greatly reducing the amount of clay in process over the older percolation systems.

A distinct effort is being made to find ways of putting clays into soap. Clay is extensively put into paper. It is now found to have distinct detergent value, and without doubt methods will be worked out for its incorporation into soap without arousing antagonism to its use.

Another contribution to the soap industry coming from the field of inorganic compounds, is the great amount of development which is going on in the field of powdered soaps by the utilization of proper combinations of soda ash, bicarbonate, tri-sodium phosphate, borax and the like. Tri-sodium phosphate particularly has been falling in price to the place where it is becoming an important possibility in such connections. Bleach manufacturers are thoroughly investigating the making of pure hypochlorites, that they may eliminate present cumbersome practice and produce stronger and more stable products.

It is stated that replacement of calcium carbonate by quick-

lime in the fluxing operations of the open hearth furnace is rapidly changing southern or high phosphorus iron to a steel basis.

The phenomenal growth of the petroleum industry is one of the outstanding developments of the present age. The great future for organic chemical investigations as a result of this is one of the good signs of the times. Production of the petroleum, however, is attended by many problems. One of these is connected with the nuisance resulting from the salt water which flows from so many wells and contaminates the streams and corrodes equipment and is a general nuisance. Now in the Mid-Continent field comes an engineering development which puts the nuisance to work, though unfortunately it will not have wide application. This is the manufacture of salt from the brine mentioned. Power plants in this same region confront the difficulty that water is sometimes scarce or unsatisfactory for condensing purposes. It has been overlooked until now that the salt brine has a great heat absorbing capacity. It is now being used for cooling and condenser purposes and upon release from the condenser at the elevated temperature into the open air drops sufficiently to release some of the salt content. As a result with proper equipment, power plant needs are supplied and salt manufacture initiated, making available a portion at least of the former waste.

V. Researches Needed to Further Inorganic Chemistry and in the Manufacture of Salts and Non-metallic Inorganic Substances.

1. Elemental carbon could probably be called an inorganic substance. At any rate its production by thermal treatment of natural gas that it may take the place of distinctly inorganic fillers in rubber and for other industrial uses is well known. Never was there a more wasteful chemical process than that in current use. The use of natural gas at all, for this purpose is destroying the patrimony of the America of our descendants. But when we think of a calculated yield of 37 lbs. of carbon per thousand cubic feet of gas, and when we actually attain a yield of 1.5 lbs. in most plants, it is evident that work is needed even though much has been done. A million dollar carbon black plant is under construction in the Amarillo oil field in the Texas Panhandle. It will handle 50,000,000 feet of residue gas a day from a casing-head gasoline plant, giving some idea of the magnitude of such manufacturing operations in this country today.

2. Corrosion Problems. Though much work has been done, there is need for a real investigation of the actual damage if any to refrigeration systems where a brine of mixed magnesium and calcium chloride is used. There are many residual brines of this type in competition with the calcium chloride from the ammonia soda process. In by-gone days the writer has found brewers saturated with the idea, that such brines gave a bromine flavor to their product. If it can be shown that magnesium is really responsible for increased corrosion in such systems, it at once becomes a question whether some simple expedient will not remedy the matter and retain the calcium-magnesium brines.

3. Bitter controversy between owners of railway water supplies and owners of coal mines whose water effluent is acid has taken the form that even neutralization with lime is doubted as a protection. Data are not available as to whether the trouble, if real, is due to magnesium, from selecting the wrong lime or whether it is due to even calcium sulfate itself. Does calcium sulfate dissociate on a boiler tube? Plaster (gypsum origin) is said to corrode iron.

4. Cottrell Fume Elimination Troubles. As a chemical engineering device the Cottrell Precipitator is well known in its successes. It is comparatively inexpensive for power plant use in throwing down ashes from the stack gases. There is a little trouble from short-circuiting the installation out of service, by the falling of the wire electrodes. Our ancient foe, the corrosion problem, accentuates this trouble with the device working on chemical fumes. Sulfuric acid fumes coming from such an installation is a common nuisance. The answer is largely engineering but partly a corrosion matter. It needs work.

5. Arc spectra, absorption spectra and X-ray studies of all the border land and complex fields of the periodic arrangement of the elements are needed.

6. An effort should be made to apply the new X-ray technique to the question of lead and other isotopes.

7. Have isotopes as a concept any relation or potential contribution to the solution of the peculiar behavior of lead in storage battery efficiency?

8. The chemistry of the addition compounds and complex derivatives formed by the oxides of nitrogen was much studied in past years, but needs a modern revamping. Such studies would assist the organic industrial chemist who is struggling for a

rubber which will withstand nitric acid for the lining of equipment.

9. We must find uses for metallic beryllium and its salts to get it down from the $200.00 per pound basis.

10. More uses for chlorine and bromine must be developed.

11. The reactions of fluorine derivatives is a field of great complexity with innumerable problems.

12. The elimination of sulfuric acid by a more direct handling of phosphate rock for available phosphoric acid should be capable of solution in more ways than electric furnace or the reoxidation of elemental phosphorus. A fuel furnacing method of breaking up this salt would be highly desirable.

13. Reasons for unsatisfactory results of American ochers in paint manufacture.

14. Careful coöperation should be organized between chemistry, mineralogy and mining for future recruiting of our mineral resources for those substances for which our engineering developments are now providing a tonnage demand and also for those substances for which the demand is of a prospective nature or also of small volume but key nature in industry. We must find more refractory material, more heat and electric insulating materials, more of selenium and tellurium and the like.

15. The analytical chemist has long overcome filtration loss of barium sulfate and other fine precipitates by the simple trick of slow digestion to allow the finer to dissolve and plate out on the coarser. It would be of material industrial interest and probably of scientific interest as well if we possessed a wider knowledge of the mechanism of the phenomenon, as to the relative importance of the factors involved, and particularly as to the distribution and intensity of the phenomenon among precipitated compounds, both inorganic and organic, such as dyes, lakes, pigments and the like. Not only is the question of loss involved but also the pestiferous separation from liquids of traces of solids which often plug filters disastrously, as well as the whole question of pigment shade and covering power.

16. Separation of certain members of the rare earth series by studying the solubility of their salts needs investigation. Crew, Steinert and Hopkins [41] state that "the solubility of salts of the rare earth metals is of special importance, because their separation depends so largely upon slight differences in solubility. In spite

[41] J. Phys. Chem., 29: 34; 1925.

of this fact there is very little accurate information available in regard to the solubility of individual salts of this group of elements."

17. Further investigation is needed of salt solutions in 100% H_2SO_4. A. W. Davidson [42] intimated that "further investigation of salt solutions in 100% H_2SO_4 might lead to discovery of interesting new compounds."

[42] J. Am. Chem. Soc., 47: 968; 1925.

Chapter XIII.

Metallo-Organic Compounds. I.

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Metallo-Organic Compounds of the 4th Group of Elements.

Lead. Organic lead compounds possess considerable technical interest because of their effectiveness as knock suppressors in internal combustion engines. Tetraethyl lead appears to be the most effective and readily available material for this purpose and, if present expectations are realized, its use will constitute the first extensive technical application of a metallo-organic compound. In any case, the work leading up to the use of tetraethyl lead as an "anti-knock" has resulted in emphasizing the importance of the scientific study of the combustion process in internal combustion engines and cannot but prove to be of the greatest importance in the future development of motor design.

Tetraethyl lead is now produced in commercial quantities. Various patents relating to its preparation, which need not be enumerated here, are appearing.

Numerous papers have appeared dealing with the mechanism of the action of knock suppressors and knock inducers and with the problem of gaseous combustion generally. As yet we have no satisfactory theory of the action of anti-knock compounds. Attention may be called to a paper by Charch, Mack and Boord,[1] who studied the electrical conductance of cylinder gases and found a relation between this quantity and the knock tendency of the original gas mixtures. They propose a theory for the action of knock suppressors which is, briefly, that the anti-knock compound decomposes forming particles of free metal throughout the volume

[1] Ind. Eng. Chem., 18: 334; 1926.

of the gas which particles, in turn, oxidize and act as centers of ignition for the mixture, this action being somewhat similar to that of multiple spark plugs. Particularly noteworthy is a paper by Clark and Thee.[2] These investigators photographed the ultraviolet spectrum of flames in engines at different portions of the stroke. This they have done for a variety of fuels in the presence and in the absence of knock inducers and knock suppressors. The nature of the fuel, as well as the presence of knock inducers or suppressors, has a marked influence on the character of the spectra obtained and this method gives promise of yielding a real insight into the mechanism of gaseous combustion. Clark, Brugmann and Thee [3] have examined the action of knock suppressors from the standpoint of the ionization theory and conclude that this theory is inadequate. Clark and Thee [4] have presented a general review of the facts and theories relating to the combustion of gaseous mixtures. A more detailed discussion of this interesting problem would be out of place here. But it may confidently be expected that we shall shortly know much more about the mechanism of the combustion process in gases than we do at the present time.

Germanium. The elements, silicon, germanium, tin and lead exhibit many properties analogous to those of carbon. The stability of the compounds of these elements, particularly toward carbon groups, increases as the atomic number diminishes. Tabern, Orndorff and Dennis [5] have supplied data with regard to the preparation and properties of a number of organic compounds of germanium. They have prepared germanium tetraphenyl, tetra-*p*-tolyl, tetrapropyl, tetra-*iso*-amyl, tetraethoxyl and tetraethyl, by means of the Grignard reagent. They give data relative to the properties of these compounds.

Tin. Kraus and Sessions [6] have prepared tin trimethyl. This compound closely resembles triphenyl methyl and allied substances. At lower concentrations in boiling benzene it exists largely in the unimolecular condition. With sodium in liquid ammonia it reacts to form sodium trimethyl stannide, $NaSn(CH_3)_3$, which is a salt-like substance, readily soluble in liquid ammonia. With the halogens, trimethyl tin combines to form compounds of the type $(CH_3)_3SnX$. Sodium trimethyl stannide is a valuable reagent

[2] Ind. Eng. Chem., 18: 528; 1926.
[3] Ind. Eng. Chem., 17: 1226; 1925.
[4] Ind. Eng. Chem., 17: 1219; 1925.
[5] J. Am. Chem. Soc., 47: 2039; 1925.
[6] J. Am. Chem. Soc., 47: 2361; 1925.

in that it reacts with many organic halides, substituting the trimethyl tin group in place of the halogen atom.

Kraus and Harada [7] have prepared and described a number of complex compounds between trimethyl tin halides and trimethyl tin hydroxides corresponding to the formulas:

$$[(CH_3)_3SnOH]_2(CH_3)_3SnX \text{ and}$$
$$(CH_3)_3SnOH(CH_3)_3SnX.H_2O.$$

Kraus and Greer [8] have investigated the free dimethyl tin group, $(CH_3)_2Sn$. It was obtained only in a polymerized condition as a yellow solid which proved to be very sensitive toward oxidizing agents. On treating dimethyl tin with sodium in liquid ammonia disodium dimethyl stannide, $Na_2Sn(CH_3)_2$, was obtained as an intensely red colored solution. Solutions of this compound are very reactive toward compounds containing halogens. On treating the salt, $Na_2Sn(CH_3)_2$, with methylene chloride they obtained the compound $H_2C=Sn(CH_3)_2$ as a highly polymerized liquid whose polymerization increases on standing.

Disodium dimethyl stannide is of particular interest as it affords a means of synthesizing compounds containing chains of tin atoms. The method may be illustrated by that employed in the preparation of a stannopentane, that is, a compound containing a chain of five tin atoms. On treating disodium dimethyl stannide with dimethyl tin dibromide the following reaction occurs:

$$2Na_2Sn(CH_3)_2 + (CH_3)_2SnBr_2 = NaSn(CH_3)_2.Sn(CH_3)_2.Sn(CH_3)_2Na + 2NaBr,$$

disodium stannopropane being formed. This is readily soluble in liquid ammonia and when treated with trimethyl tin bromide reaction takes place as follows:

$$Na(CH_3)_2Sn.(CH_3)_2Sn.(CH_3)_2SnNa + 2(CH_3)_3SnBr = (CH_3)_3Sn.(CH_3)_2Sn.(CH_3)_2Sn.(CH_3)_2Sn.Sn(CH_3)_3 + 2NaBr.$$

The completely methylated stannopentane is moderately stable toward oxidation and is readily soluble in organic liquids and yields a normal molecular weight in benzene solution.

Chambers and Scherer [9] have investigated the phenyl tin derivatives. They prepared sodium triphenyl stannide and disodium diphenyl stannide in liquid ammonia solution, both compounds

[7] J. Am. Chem. Soc., 47: 2416; 1925.
[8] J. Am. Chem. Soc., 47: 2568; 1925.
[9] J. Am. Chem. Soc., 48: 1054; 1926.

being readily soluble with characteristic color. Employing these compounds as reagents they have prepared triphenyl stannane, $(C_6H_5)_3SnH$, triphenyl tin acetic acid, $(C_6H_5)_3SnCH_2COOH$ and diphenyl tin, $(C_6H_5)_2Sn$. The latter compound, it is interesting to note, was obtained as a decomposition product of the dihydride $(C_6H_5)_2SnH_2$ which decomposed just above liquid ammonia temperatures according to the equation:

$$(C_6H_5)_2SnH_2 = (C_6H_5)_2Sn + H_2.$$

Particularly interesting is the fact that the diphenyl tin so obtained is unimolecular in benzene solutions, although polymerization occurs on standing. It is interesting, too, to note that triphenyl stannane oxidizes with the formation of triphenyl tin according to the equation:

$$2(C_6H_5)_3SnH + \tfrac{1}{2}O_2 = 2(C_6H_5)_3Sn + H_2O.$$

Kraus and Rosen[10] prepared triphenyl stannyl amine, $(C_6H_5)_3SnNH_2$, through the ammonolysis of the corresponding chloride.

Pharmacology. With the exception of lead, but little attention has been paid to the pharmacology of organic derivatives of the elements of the fourth group. Tetraethyl lead, in particular, has received considerable attention during the past year as regards its toxic effects. Reference might here be made to the report of the Surgeon General's Committee.[11] According to recent work of D. E. Jackson of the College of Medicine at the University of Cincinnati (the results of which have not as yet been published), organic tin compounds are highly toxic, having a marked influence on the respiratory tract.

This brief sketch of the elements of the fourth group shows clearly that an extensive chemistry of these elements remains to be developed, particularly in the case of germanium and silicon, whose compounds, generally, are very stable. Boron might properly have been included in the present discussion, but no work relating to organic boron compounds has been published during the past year. The chemistry of boron will probably prove even more interesting than that of the elements of the fourth group. Organic derivatives of aluminum and thallium also present many points of interest. Aside from the organic derivatives of mercury

[10] J. Am. Chem. Soc., 47: 2739; 1925.
[11] Ind. Eng. Chem., 18: 193; 1926.

and of the elements of the fifth group which have been extensively investigated because of their possible therapeutic value, the organic derivatives of metallic elements have been much neglected in this as in most other countries. The chemistry of these elements cannot be seen in proper perspective until we shall have gained a comprehensive and comparative knowledge of the compounds of these elements with hydrocarbon groups as well as with other groups and elements.

Chapter XIV.

Metallo-Organic Compounds. II.

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Compounds of Arsenic, Antimony, and Bismuth.

During the year there has been the usual very large amount of pharmacological and clinical work on arsphenamine and related substances. The only outstanding work on aliphatic arsenicals is that on the β-chlorovinylarsines.[1] In the aromatic series arsenic derivatives have been prepared from diaminophenylarsonic acid [2] and the isomeric diaminoarsenobenzenes.[3] The action of alkyl chlorocarbonates on hydroxy-aryl-arsenic acids has been studied.[4] A new type of arsenicals is represented in 2,3-dicarboxyphenylarsonic acid.[5] Various phthaleins have been coupled with diazotized *p*-arsanilic acid.[6] In the heterocyclic series studies have been made on arsono-cinchophen,[7] on various phenylbenzothiazole arsonic acids,[8] and on arsine tri-1-piperidinium chloride.[9] Certain arsenic derivatives of -onium compounds related to choline have been prepared.[10]

The purely chemical work on antimony and bismuth compounds has been limited to studies of the action of polyhydric phenols with sodium antimonyl tartrate [11] and an extensive study of triaryl bismuth dihalides including a tricarboxylic acid.[12] The

[1] Lewis and Stiegler, J. Am. Chem. Soc., **47**: 2546; 1925.
[2] Lewis and Bent, J. Am. Chem. Soc., **48**: 949; 1926.
[3] Kashima, J. Am. Chem. Soc., **47**: 2207; 1925.
[4] Hamilton and Johnson, J. Am. Chem. Soc., **48**: 1405; 1926.
[5] Hamilton and Frazier, J. Am. Chem. Soc., **48**: 2414; 1926.
[6] Christiansen, J. Am. Chem. Soc., **47**: 2244; 1925.
[7] Calvery, Noller, and Adams, J. Am. Chem. Soc., 47: 3058; 1925.
[8] Bogert and Corbitt, Proc. Nat. Acad. Sci., **11**: 768; 1925.
[9] Leonard, J. Pharmacol., **28**: 233; 1926.
[10] Renshaw and Ware, J. Am. Chem. Soc., **47**: 2989; 1925.
[11] Christiansen, J. Am. Chem. Soc., **48**: 1365; 1926.
[12] Supniewski and Adams, J. Am. Chem. Soc., **48**: 507; 1926.

use of various bismuth compounds in the therapy of syphilis has been the subject of many studies during the year.

Compounds of Mercury, Magnesium, and Gold.

As usual the work on organic mercury compounds has been mainly in the aromatic series. The few articles in the aliphatic series include one on mercury derivatives of various substituted acetylenes [13] and a method for identifying primary aliphatic halides by changing them to the Grignard compounds and then to the corresponding alkyl mercuric bromides, which are easy to purify and have definite melting points.[14] Among the simpler aromatic mercury studies are those on the action of mercury diphenyl with acyl halides in which ketones are formed,[15] the formation of phenylmercuriamide from the iodide and potassium amide,[16] the preparation and properties of chloromercuri-benzoic acid,[17] and the mercury derivatives of toluene sulfonic acid.[18] In the field of dyes and related substances mercury derivatives have been prepared both from mercurated intermediates [19] and by the direct mercuration of dyes.[20,21] Mercury derivatives of selenophenes have been prepared in much the same way as from the thiophenes.[22] The two articles which stand out with special theoretical interest are those on the use of unsymmetrical mercuri-bis compounds with hydrochloric acid to determine the relative polarity of various organic radicals [23] and the isolation of optically active organic mercury compounds from the reaction products of mercuric salts with *l*-menthyl cinnamate.[24] An extensive study has been made of the various complex salts formed from quinoline and mercuric salts.[25]

A large amount has appeared on the reactions of the Grignard reagent. Besides the numerous articles on its more ordinary uses in synthesis, there have been articles on its action on aryl sulfonates,[26] azobenzene,[27] organic peroxides,[28] and aromatic

[13] Johnson and McEwen, J. Am. Chem. Soc., 48: 469; 1926.
[14] Marvel, Gauerke, and Hill, J. Am. Chem. Soc., 47: 3009; 1925.
[15] Calvery, J. Am. Chem. Soc., 48: 1009; 1926.
[16] Chambers and Scherer, J. Am. Chem. Soc., 48: 1057; 1926.
[17] Whitmore and Woodward, J. Am. Chem. Soc., 48: 533; 1926.
[18] Whitmore and Ehrenfeld, J. Am. Chem. Soc., 48: 789; 1926.
[19] Whitmore, Hanson, and Leuck, J. Am. Chem. Soc., 48: 1013; 1926.
[20] Proskouriakoff and Raiziss, J. Am. Chem. Soc., 47: 1974; 1925.
[21] Chalkley, J. Am. Chem. Soc., 47: 2055; 1925.
[22] Bogert and Andersen, J. Am. Chem. Soc., 48: 223; 1926.
[23] Kharasch and Grafflin, J. Am. Chem. Soc., 47: 1948; 1925.
[24] Sandborn and Marvel, J. Am. Chem. Soc., 48: 1409; 1926.
[25] Dehn, J. Am. Chem. Soc., 48: 277; 1926.
[26] Gilman, Beaber, and Myers, J. Am. Chem. Soc., 47: 2047; 1925.
[27] Gilman and Pickens, J. Am. Chem. Soc., 47: 2406; 1925.
[28] Gilman and Adams, J. Am. Chem. Soc., 47: 2816; 1925.

isothiocyanates.[29, 30] Further studies have been made on the luminescent properties of certain Grignard reagents.[31] New theories as to the structure of the Grignard reagent have also been advanced.[32, 33]

A general method for making carbon-gold compounds has been perfected.[34]

[29] Worrall, J. Am. Chem. Soc., **47**: 2974; 1925.
[30] Gilman and Wood, J. Am. Chem. Soc., **48**: 806; 1926.
[31] Evans and Diepenhorst, J. Am. Chem. Soc., **48**: 715; 1926.
[32] Gilliland and Blanchard, J. Am. Chem. Soc., **48**: 410; 1926.
[33] Boord and Sung, "A Theory of the Grignard Reaction," presented at the Philadelphia meeting of A. C. S., Sept., 1926.
[34] Kharasch, "Direct Auration," presented at the Philadelphia meeting of A. C. S., Sept., 1926.

Chapter XV.

Aliphatic Compounds.

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The papers that come under this head are surprisingly numerous, 53 in The Journal of the American Chemical Society for the year 1925-1926. As the number is so large and the space available is limited, no attempt has been made to do more than indicate the contents of each article. For convenience the articles have been divided into groups.

Identification and Estimation.

There are so many organic compounds known and there are so many mixtures in which they may occur that methods of identification and estimation are always welcome. Marvel, Gauerke and Hill [1] bring forward a method by which crystalline compounds having satisfactory melting points are conveniently obtained from primary alkyl bromides and iodides. The alkyl bromide or iodide is made to react with magnesium and the resulting Grignard reagent is treated with the corresponding mercuric halide.

Johnson and McEwen,[2] also of the University of Illinois, have prepared the mercuric derivatives of a wide variety of monoacetylenes, $R-C:CH$. These have the general formula $(R.C:C)_2Hg$ and are well defined stable compounds with characteristic melting points.

Acetic anhydride has been a difficult substance to assay accurately. Whitford [3] finds that it can be exactly and quickly determined by a gasometric method depending on the reaction:

$$(COOH)_2 + (CH_3CO)_2O \longrightarrow CO + CO_2 + 2CH_3COOH.$$

[1] J. Am. Chem. Soc., 47: 3009; 1925.
[2] J. Am. Chem. Soc., 48: 469; 1926.
[3] J. Am. Chem. Soc., 47: 2939; 1925.

As the dehydration of the oxalic acid depends on the amount of anhydride, it is a direct method. The reaction is carried out in dry pyridine.

As preparation for studies in partition, Munch [4] has made elaborate measurements of the refractive indices of solutions of methyl, ethyl, propyl, isopropyl, the four butyl and three amyl alcohols and their formates, acetates, propionates, butyrates and isovalerates in water and cottonseed oil. It is found that accurate determinations may be made by this method.

Phelps and Rowe [5] have examined the methods that have been proposed for the estimation of aldehyde in ether and have found one based on the use of Schiff's reagent to be the best. They have standardized this so that amounts of aldehyde around 0.003% may be estimated.

As a possible basis for the identification of classes of organic compounds, the infra-red absorption of ethers, esters and related substances has been studied by Smith and Boord.[6] The relative intensities of the bands change with alteration of structure but their positions remain essentially the same.

Determination of the Properties of Organic Substances.

We say that we know more than 200,000 organic compounds but our acquaintance with the vast majority of them is exceedingly slight. Of only a few do we know the properties with satisfactory exactness and certainty. There are endless opportunities for useful work in determining the properties of substances. Valuable results may be obtained in this field by a relatively inexperienced investigator, provided he has much patience and a love for accuracy, yet the most adroit veteran can find tasks worthy of his best efforts. We find American chemists active in this field.

Taylor and Rinkenbach [7] have made careful determinations on the melting point and vapor pressure of glycol diacetate. They have measured the solubility of a number of substances in it and its solubility in various liquids.

The solubilities of glycol ethers in water have been investigated by Cox and Cretcher,[8] who find for some of them closed curves similar to the solubility curve of nicotine and water.

[4] J. Am. Chem. Soc., 48: 994; 1926.
[5] J. Am. Chem. Soc., 48: 1049; 1926.
[6] J. Am. Chem. Soc., 48: 1512; 1926.
[7] J. Am. Chem. Soc., 48: 1305; 1926.
[8] J. Am. Chem. Soc., 48: 451; 1926.

Williams [9] has studied the specific heat, vapor pressure, density and absorption spectrum of nitromethane with the hope that its suspected tautomerism might be betrayed. Some irregularities were detected in the temperature coefficient of the specific heat.

Perry and Bardwell [10] have made careful measurements of the vapor pressure of solid and liquid cyanogen and Perry and Porter [11] have similarly studied hydrocyanic acid.

The mutual solubility relations of *n*-butyl alcohol and water have been studied by Hill and Malisoff.[12]

Parks and Anderson [13] have measured the heat capacities, entropies and free energies of *tert.*-butyl alcohol, mannitol, erythrytol and *n*-butyric acid.

Germann and Taylor [14] have measured the vapor tension of phosgene from 0° to 181.6°, which they find to be the critical temperature.

Smyth and Zahn [15] have measured the dielectric constants of ethane, ethylene, acetylene and butylene with the object of finding out something as to the symmetry of unsaturated bonds.

The peculiarities of barium lactate with regard to crystallization have been thoroughly investigated by Krauskopf and Carter [16] who conclude that lactide is present in acid or neutral solution and hinders crystallization.

Wing and Thompson [17] have determined the solubility of barium propionate at various temperatures from 0° to 100°, and find a minimum at 10°.

Weatherby, McIlvaine and Matlin [18] find that tributyrin boils at 305-10° instead of 285°, the accepted value.

Determination of Composition and Constitution of Natural Substances.

This was the chief occupation of organic chemists in early times. Many problems of this sort remain. We find nine papers in this field.

Marvel and Broderick [19] have made a study of the "yellow oil" which is obtained as a by-product in the manufacture of butyl

[9] J. Am. Chem. Soc., 47: 2644; 1925.
[10] J. Am. Chem. Soc., 47: 2629; 1925.
[11] J. Am. Chem. Soc., 48: 299; 1926.
[12] J. Am. Chem. Soc., 48: 924; 1926.
[13] J. Am. Chem. Soc., 48: 1506; 1926.
[14] J. Am. Chem. Soc., 48: 1154; 1926.
[15] J. Am. Chem. Soc., 47: 2501; 1925.
[16] J. Am. Chem. Soc., 48: 1474; 1926.
[17] J. Am. Chem. Soc., 48: 104; 1926.
[18] J. Am. Chem. Soc., 47: 2249; 1925.
[19] J. Am. Chem. Soc., 47: 3045; 1925.

alcohol by fermentation and have identified a number of its constituents.

The unsaturated fatty acids associated with corn starch have been found by Taylor and Lehrman [20] to be oleic and linoleic acids.

Citric, malic and malonic acid have been found in notable amounts in alfalfa by Turner and Hartman.[21]

Tanaka and Nagai [22] have investigated the naphthenic acids found in Akita-Kurokawa petroleum and have isolated and characterized four acids, $C_{12}H_{22}O_2$, $C_{13}H_{24}O_2$, $C_{14}H_{26}O_2$ and $C_{15}H_{28}O_2$.

Preparations.

The preparation of compounds has ever been important with organic chemists. We find seven papers in this class running from simple to complex. Many new compounds need to be prepared to extend series or fill in gaps. Few preparation methods have been so well worked out that there is not room for improvement.

Wood [23] purifies alkyl sulfides with finely divided copper.

Youtz [24] gives us a rapid method for obtaining cetyl alcohol.

Farren, Fife, Clark and Garland [25] have prepared a number of new chloromethyl ethers and have used them to make alkoxymethyl esters.

Noller and Adams [26] have obtained aldehyde esters by ozonizing methyl esters of unsaturated acids.

Goebel [27] has synthesized several derivatives of citraconic acid.

Jones and Burns [28] have prepared a number of amines containing one or more hydroxyethyl groups.

Oesper, Broker and Cook [29] have converted ethylene and trimethylene glycols into chlorocarbonates and carbamates.

Reactions of Compounds.

We find eight papers in this class. As each of the more than 200,000 organic compounds may undergo many reactions, there are endless possibilities in this field.

[20] J. Am. Chem. Soc., 48: 1739; 1926.
[21] J. Am. Chem. Soc., 47: 2044; 1925.
[22] J. Am. Chem. Soc., 47: 2369; 1925.
[23] J. Am. Chem. Soc., 47: 2062; 1925.
[24] J. Am. Chem. Soc., 47: 2252; 1925.
[25] J. Am. Chem. Soc., 47: 2419; 1925.
[26] J. Am. Chem. Soc., 48: 1074; 1926.
[27] J. Am. Chem. Soc., 47: 1990; 1925.
[28] J. Am. Chem. Soc., 47: 2966; 1925.
[29] J. Am. Chem. Soc., 47: 2609; 1925.

West [30] has studied the condensation of glyoxal with aceto-acetic ester with the hope of throwing light on the oxidation of ketones in human metabolism.

The electrolytic reduction of acrolein has been investigated by Read and Freer,[31] who find Δ^1-cyclopentane aldehyde among the products.

Sanborn and Marvel [32] find that the products formed by the addition of mercury salts to olefins are true compounds.

The addition of iodine to acetylene derivatives has been found to be a bimolecular reaction by Miss Eichelberger.[33] The preparation of di-iodofumaric acid has been worked out.

The decomposition of oxalic acid by acetic anhydride has been studied by Whitford.[34] The reaction is complete in the presence of pyridine.

Moses and Reid [35] find that an alkyl disulfide reacts with two atoms of sodium to form two molecules of sodium mercaptide.

Fry and Schulze [36] have investigated the liberation of hydrogen in the action of fused caustic alkalies on organic compounds.

The addition of cyanoacetic esters to esters of glutaconic and β-methylglutaconic esters has been studied by Kohler and Reid [37] with reference to the isomers that may be present.

Investigations Grouped Around Certain Compounds.

In a number of cases some compound is taken as the starting point in an investigation, its reactions and derivatives being worked out. This is a good way to investigate. The chemist gets a supply of almost anything and goes to work to find what he can make out of it.

Nau, Brown and Bailey [38] start with methylene-citric anhydride and prepare a large number of derivatives from it.

Dimethylglyoxime has been taken up by Semon and Damerell [39] and its preparation simplified. The methods for related compounds have also been improved.

The preparation and properties of some esters of ethylhexyl-acetic acid are given by Dox.[40]

[30] J. Am. Chem. Soc., 47: 2780; 1925.
[31] J. Am. Chem. Soc., 48: 1401; 1926.
[32] J. Am. Chem. Soc., 48: 1409; 1926.
[33] J. Am. Chem. Soc., 48: 1320; 1926.
[34] J. Am. Chem. Soc., 47: 2934; 1925.
[35] J. Am. Chem. Soc., 48: 776; 1926.
[36] J. Am. Chem. Soc., 48: 958; 1926.
[37] J. Am. Chem. Soc., 47: 2803; 1925.
[38] J. Am. Chem. Soc., 47: 2596; 1926.
[39] J. Am. Chem. Soc., 47: 2033; 1925.
[40] J. Am. Chem. Soc., 47: 3008; 1925.

Alcohols containing the trichloromethyl group have been studied by Howard.[41]

Lawson and Reid [42] have investigated the reactions of mustard gas and its oxidation products with amines in the hope of throwing some light on its toxic action.

Ethyl selenomercaptan has been the starting point for the preparation of a number of compounds by Shaw and Reid.[43]

Constitution and Properties.

The relation of properties to constitution is always of interest to the organic chemist. In fact a better understanding of the connection between the two is the underlying motive for most of his investigation. Many more data of this sort are required.

Renshaw and Ware [44] have continued the study of choline derivatives in a search for the basis of the physiological activity of the members of this group.

Stewart and Aston [45] have measured the dissociation constants of amino ethers to find the effect of oxygen on the basicity of amines.

Theory of Organic Compounds and Reactions.

The weakness of organic chemistry is lack of insight into why things are as they are. Organic chemists are beginning to apply the newer methods of subatomic investigation to these problems.

Noyes [46] has studied the fifth valence of nitrogen in the tetraalkyl ammonium salts, applying what is known of the arrangements of electrons, and finds that it is a real polar valence.

Huggins and Hendricks [47] have reinvestigated the crystal structure of pentaerythrite and agree with Mark and Weissenberg [48] that the four surrounding carbon atoms lie in a plane, at the corners of a square and not at the vertices of a tetrahedron. This calls attention to the need for similar investigations of many other carbon compounds to see how far the tetrahedron theory applies or how it must be modified.

A solitary paper on equilibrium may be put under this heading. Evans and Nicoll [49] have considered the acetone-isoacetone

[41] J. Am. Chem. Soc., **48**: 774; 1926.
[42] J. Am. Chem. Soc., **47**: 2821; 1925.
[43] J. Am. Chem. Soc., **48**: 520; 1926.
[44] J. Am. Chem. Soc., **47**: 2989; 1925.
[45] J. Am. Chem. Soc., **48**: 1642; 1926.
[46] J. Am. Chem. Soc., **47**: 3025; 1925.
[47] J. Am. Chem. Soc., **48**: 164; 1926.
[48] Z. Physik., **17**: 301; 1923.
[49] J. Am. Chem. Soc., **47**: 2789; 1925.

RESEARCH BY INSTITUTIONS.

Universities and Colleges	Types of Compounds	Investigators
California	Amines	T. D. Stewart, J. G. Aston
California Inst. Tech.	Structure of molecules	M. L. Huggins, S. B. Hendrik
Cincinnati	Alcohols and esters	H. S. Fry, Else L. Schulze
	Chlorocarbonates	R. E. Oesper, W. Broker, W. A. Cook
Columbia	Unsatd. fatty acids	T. C. Taylor, L. Lehrman
Harvard	Glutaminic acids	E. P. Kohler, G. H. Reid
Illinois	Chaulmoogric acid	Roger Adams, C. R. Noller, R. L. Shriner
	Amines	W. A. Noyes
	Identification of halides	C. S. Marvel, C. G. Gauerke, E. L. Hill
	Butyl alcohol fermentation	C. S. Marvel, A. E. Broderick
	Acetylenes	J. R. Johnson, W. L. McEwen
	Aldehyde-esters	Roger Adams, C. R. Noller
	Olefins	C. S. Marvel, L. T. Sanborn
Johns Hopkins	Mustard gas	W. E. Lawson, E. E. Reid
	Selenomercaptans	E. H. Shaw, Jr., E. E. Reid
	Alkyl disulfides	Mrs. C. G. Moses, E. E. Reid
Mississippi	Alkyl sulfides	A. E. Wood
Montana	Trichloromethyl group	J. W. Howard
Nebraska	Propionates	H. J. Wing, T. J. Thompson
New York	Butyl alcohol	A. E. Hill, W. M. Malisoff
	Chlorine derivatives	R. R. Renshaw, J. C. Ware
Ohio State	Acetone	W. L. Evans, W. D. Nicoll
	Infra-red absorption	C. E. Boord, A. W. Smith
Princeton	Substituted amines	L. W. Jones, G. R. Burns
S. California	Butyrin	L. S. Weatherby, Lillian McIlvaine, D. Matlin
Stanford	Chaulmoogra oil	T. Hashimoto
	Phosgene	A. O. F. Germann, Q. W. Taylor
	Thermal data	G. S. Parks, C. T. Anderson
Texas	Methylenecitric acid	J. R. Bailey, C. A. Nau, E. B. Brown
Vermont	Acrolein	R. R. Reid, R. M. Freer
Washington	Dimethylglyoxime	W. L. Semon, V. R. Damerell
Washington Sch. Med.	Glyoxal	E. S. West
W. Virginia	Chloro-ethers	F. E. Clark, C. E. Garland, J. W. Farren, H. R. Fife
Wisconsin	Acetic anhydride	E. L. Whiteford
	Nitromethane	J. W. Williams
	Lactates	F. C. Krauskopf, A. S. Carter

RESEARCH BY INSTITUTIONS.—*Continued.*

Research Institutes, Etc.	Types of Compounds	Investigators
Bureau of Chemistry.	Alcohols and esters	J. C. Munch
Bureau of Dairying..	Alfalfa	W. A. Turner, A. M. Hartman
Bureau of Mines....	Cyanogen	J. H. Perry, D. C. Bardwell
	Hydrocyanic acid	J. H. Perry, F. Porter
	Glycol diacetate	C. A. Taylor, W. H. Rinkenbach
Chicago Munic. Tuber. Sanit.	Acetylene derivs.	Lillian Eichelberger
Mass. Homeop. Hospital	Ether	E. A. Phelps, A. W. Rowe
Mellon Inst.	Glycol ethers	H. L. Cox, L. H. Cretcher
Philippine Health Ser.	Chaulmoogric acid	G. A. Perkins
Rockefeller Inst.	Citraconic acid derivs.	W. A. Goebel
Industrial Laboratories		
Parke, Davis & Co...	Ethylhexylacetic acid	A. W. Dox
Standard Oil, Ind....	Cetyl alcohol	M. A. Yoletz

equilibrium. The nature of the oxidation products of acetone depends on the alkalinity of the solution. This is well explained by showing that the above equilibrium is shifted by alkali.

The widespread interest in research on aliphatic compounds is shown by the distribution of workers as brought out in the table on page 107.

Some Suggested Problems.

In each section of this review of research the need of investigation in that line is pointed out. Identification methods are unsatisfactory or lacking for whole series of aliphatic compounds. When the physical constants for the members of series of compounds are accurately determined we will be in a position to work out mathematical relations and evaluate the effects on these properties of the introduction of substituents. The reactions of aliphatic compounds are by no means as well known as are those of the aromatic.

The outstanding need in aliphatic chemistry is to find methods for initiating and controlling reactions with paraffin hydrocarbons. The pure hydrocarbons up to *n*-hexane can now be obtained in

quantity from natural gas petroleum. Oxygen derivatives of these are extremely valuable but getting the oxygen in and placing it properly is at present beyond us, except in a few special cases. Useful progress has been made in the chlorination of these hydrocarbons but this is only a beginning.

The possible reactions of unsaturated hydrocarbons are many. Our knowledge of them is far too fragmentary.

The most spectacular recent event in chemistry has been the methanol synthesis. This raises the question of other high temperature, high pressure syntheses.

Secondary and tertiary alcohols along with the corresponding chlorides are now available. These give opportunities for scientific study and industrial applications.

Chapter XVI.

Carbocyclic Series.

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A review of the researches in carbocyclic chemistry published during the past year in the United States is rendered particularly difficult because of the fact that "vat dyes and intermediates," "azo dyes and intermediates," "medicinals," "pharmaceutical chemistry," "explosives," and "catalysts" are to be considered in separate chapters. It is surprising to note how large a proportion of the published research on carbocyclic chemistry has as its ultimate goal some substance of value to medicine or of value as a dye, or falls under one of the headings mentioned. As the results of most of these papers are of interest at present chiefly from the standpoint of pure organic chemistry, the writer feels it desirable at least to mention them.

A second difficulty arises in the interpretation of whether a molecule containing an aromatic residue should be included in this review, when the primary interest in the study of such compounds may lie entirely in the reactivity of an aliphatic residue present in the molecule. Those papers are discussed, therefore, in which the compounds described contain aromatic groups essential to the reactivity of the molecule.

While few papers of general interest have appeared, there is real value in a review which will indicate the general lines of work which have been pursued in various universities and technical laboratories, and a particular effort will be made to cover these points as thoroughly as the limited space will allow. Papers in similar fields of research will be grouped together for discussion.

Work upon carbocyclic compounds other than those which contain an aromatic residue has been very limited in character. Shriner and Adams [1] at the University of Illinois have made a

[1] J. Am. Chem. Soc., 47: 2727; 1925

careful study of the older and of new reactions of chaulmoogric acid and have shown that Powers and his collaborators, who did the pioneer work on the constitution of chaulmoogric acid, were not entirely correct in the structure they assigned to this acid. Shriner and Adams concluded that 13-(Δ^2-cyclopentenyl)-tridecanoic acid represents all the known facts concerning chaulmoogric acid. In continuation of the work in this field Noller and Adams [2] reduced chaulmoogric and hydnocarpic acids catalytically to the corresponding dihydro compounds and then synthesized these latter substances by the action of the proper cyclic Grignard reagents upon the proper aliphatic aldehyde esters and finally saponification and reduction of the hydroxy esters produced. Thus, dihydrochaulmoogric acid was prepared from cyclopentyl magnesium bromide according to the following equation:

$$\begin{array}{l} CH_2-CH_2 \\ | \qquad > CHMgBr + CHO-(CH_2)_{11}-CO_2CH_3 \longrightarrow \\ CH_2-CH_2 \end{array}$$

$$\begin{array}{l} CH_2-CH_2 \\ | \qquad > CH-CHOH-(CH_2)_{11}-CO_2CH_3 \longrightarrow \\ CH_2-CH_2 \end{array}$$

$$\begin{array}{l} CH_2-CH_2 \\ | \qquad > CH-(CH_2)_{12}-CO_2H \\ CH_2-CH_2 \end{array}$$

The necessary aldehyde esters were prepared by the ozonation of various esters of certain unsaturated fatty acids.[3]

The observation that dihydrochaulmoogric and dihydrohydnocarpic acids were bactericidal toward *B. leprœ* led Hiers and Adams [4] to a study of the synthesis of homologous acids containing a cyclohexyl group in place of the cyclopentyl group. These substances proved to be bactericidal and confirmed the assumption that the ring structure has an important part to play in the therapeutic effect of the molecule. Perkins [5] at the Culion Leper Colony in the Philippines has prepared certain chaulmoogric acid derivatives, particularly dihydroxychaulmoogric acids by oxidation of chaulmoogric acid in the hope of obtaining substances of a greater therapeutic effect than chaulmoogric acid itself.

Hashimoto [6] at Leland Stanford University investigated the

[2] J. Am. Chem. Soc., **48**: 1080; 1926.
[3] J. Am. Chem. Soc., **48**: 1074; 1926.
[4] J. Am. Chem. Soc., **48**: 1089; 1926.
[5] J. Am. Chem. Soc., **48**: 1714; 1926.
[6] J. Am. Chem. Soc., **47**: 2325; 1925.

highest boiling acids in chaulmoogra oil. By distillation at very low pressures of the ethyl esters he was able to isolate in the pure state (although he has not identified them) several new acids probably cyclic in character, containing one or more olefine linkages.

Interesting and important investigations on free radicals have been continued by Gomberg and his associates at the University of Michigan, and new work in this field has just been developed by Conant and his associates at Harvard University. Gomberg and Forrester [7] have described various new dimethoxy substituted triphenylmethyls and their properties and the formation of certain methoxytetraaryl methanes. Gomberg and McGill [8] have shown that *o*-hydroxytriaryl carbinols containing naphthyl groups are tautomeric substances. Further evidence that free radicals exist to a certain extent in the quinonoid form is offered. Gomberg and Tabern [9] have described certain halogen substituted acridyls and have demonstrated the peculiar activity of the halogens, due presumably to quinoidation.

Perhaps the most outstanding work which has been published during the past year, and certainly the most important work in the field of triarylmethyls for several years, is that of Conant and his associates. Conant, Small and Taylor [10] have shown that triaryl carbinols in acid solution can readily be reduced directly by means of vanadous chloride to dissociated and undissociated ethanes. The investigation has shown that a mixture of free radical and the corresponding halochromic salt has a definite potential, and the single electrode potential of various radicals under different conditions has been determined. Conant and Small [11] have applied the vanadous chloride reduction method to the preparation of various dixanthyl derivatives. It was possible to demonstrate that dicyclohexyl dixanthyl dissociates to a considerable extent in solution, thus indicating the effectiveness of an alicyclic group in promoting dissociation. Conant, Small and Sloan [12] have extended the study to the preparation of various dialkyl dixanthyls. Apparently di-*sec.*-alkyl dixanthyls, such as di-isopropyl or di-*sec.*-butyl dixanthyls, have a definite tendency to dissociate in solution, while the di-primary alkyl dixan-

[7] J. Am. Chem. Soc., 47: 2373; 1925.
[8] J. Am. Chem. Soc., 47: 2392; 1925.
[9] J. Am. Chem. Soc., 48: 1345; 1926.
[10] J. Am. Chem. Soc., 47: 1959; 1925.
[11] J. Am. Chem. Soc., 47: 3068; 1925.
[12] J. Am. Chem. Soc., 48: 1743; 1926.

thyls have little or none. Conant and Cutter [13] have used vanadous chloride for the reduction of aromatic aldehydes in acid solution. The authors conclude that probably halochromic salts of the aldehydes are formed as intermediates.

A very popular field for work has been among the metallo-organic compounds, particularly compounds of mercury, arsenic, antimony, bismuth, germanium, and of tin as well as of organo-magnesium compounds. The ultimate object in the study of the first five mentioned metallic derivatives has been, with one or two exceptions, to prepare compounds of medicinal importance. These are discussed in the chapters on "Metallo-Organic Compounds."

A search for new anæsthetics of various types has led to a number of published researches during the past year. Cretcher and Pittenger [14] at Mellon Institute have prepared the glycol esters of various aromatic acids, in particular that of *p*-amino-benzoic acid, but it showed no anæsthetic value. Hill and Rabinowitz [15] at Yale University have made several new anæsthetics of the holocaine type. Adams, Rideal, Burnett, Jenkins and Dreger [16] at the University of Illinois made a careful study of the relation between physical constants, chemical constitution and physiological action of a series of alkyl *p*-aminobenzoates. The physiological action toward goldfish ran parallel to the surface tension effect and to the distribution coefficient between amyl acetate and water. It was noted that the physiological action in this series increased with the increased size of the alkyl group, and the *n*-alkyl derivatives were more effective than their isomeric derivatives. Case [17] at Harvard University prepared certain esters of *p*-ethoxymethylbenzoic acid and certain esters of 4-hydroxymethyl-3-aminobenzoic acid. Barkenbus and Holtzclaw [18] at the University of Kentucky have prepared some new esters of *o*-cyanobenzyl alcohol and *p*-carboxybenzyl alcohol.

The remarkable publicity which has been given to the use of hexylresorcinol as an internal urinary antiseptic, has resulted in the publication of a number of articles in this field. Dohme, Cox and Miller [19] of Sharpe and Dohme who made the original

[13] J. Am. Chem. Soc., **48**: 1016; 1926.
[14] J. Am. Chem. Soc., **47**: 2560; 1925.
[15] J. Am. Chem. Soc., **48**: 732; 1926.
[16] J. Am. Chem. Soc., **48**: 1758; 1926.
[17] J. Am. Chem. Soc., **47**: 3003, 3005; 1925.
[18] J. Am. Chem. Soc., **47**: 2189; 1925.
[19] J. Am. Chem. Soc., **48**: 1688; 1926.

discovery, have published the preparation and the comparative antiseptic effects of various alkyl resorcinols indicating the relative outstanding values of the hexylresorcinol as compared with the others. Klarmann [20] of the Lehn and Fink Laboratories has described benzyl and β-phenylethylresorcinols and Klarmann and Figdor [21] have prepared certain new alkyl and aryl phloroglucinols.

In the field of catalytic reduction, Hiers and Adams [22] at the University of Illinois have described the reduction of various aromatic amines by means of hydrogen and platinum-oxide platinum black. Tuley and Adams [23] have shown that by means of this same catalyst with the addition of small amounts of zinc acetate and ferrous chloride, cinnamic aldehyde could be reduced quantitatively to cinnamyl alcohol without reduction of the olefine group. Carothers and Jones [24] at the same laboratory used hydrogen and platinum-oxide platinum black to reduce aromatic nitriles in the presence of acetic anhydride to give exclusively the acetyl derivative of primary amines without the usual formation of secondary amines. Parrett and Lowy [25] have studied the reduction of α-nitronaphthalene to α-naphthylamine, with platinum-oxide platinum black, palladium-oxide palladium black, nickel, and other catalysts under various conditions of solvent, temperature, etc. Schulze and Lochte [26] in continuation of their work on the reduction of azines have described the reduction of the azine of acetophenone to *sym* dimethylphenylmethylhydrazine.

Almost every year new suggestions appear for the identification of different types of organic compounds. Nicolet and Sacks [27] suggest the use of 3-nitrophthalic anhydride for alcohols; Wheeler and Walker [28] the use of 4-(*m*-nitrophenyl)-semicarbazide for ketones; Bickel and French [29] the use of α-naphthyl isocyanate for alcohols and French and Wirtel [30] the same reagent for phenols and amines.

Wales and Palkin,[31] as a means of identifying phenols, have

[20] J. Am. Chem. Soc., **48**: 791; 1926.
[21] J. Am. Chem. Soc., **48**: 803; 1926.
[22] Ber., **59**: 162; 1926.
[23] J. Am. Chem. Soc., **47**: 3061; 1925.
[24] J. Am. Chem. Soc., 47: 3051; 1925.
[25] J. Am. Chem. Soc., **48**: 778; 1926.
[26] J. Am. Chem. Soc., **48**: 1030; 1926.
[27] J. Am. Chem. Soc., **47**: 2348; 1925.
[28] J. Am. Chem. Soc., **47**: 2792; 1925.
[29] J. Am. Chem. Soc., **48**: 747; 1926.
[30] J. Am. Chem. Soc., **48**: 1736; 1926.
[31] J. Am. Chem. Soc., **48**: 810; 1926.

converted them into azo dyes and have then examined these dyes in water, alcohol, and acetone solutions spectroscopically. The absorption spectra maxima for these various dyes are reported. In many cases, however, the values do not appear to be very characteristic.

Very little work has ever been done upon the infra-red absorption spectra of organic compounds, but now a systematic research has been started by Bell [32] in the Pharmacology Department of Johns Hopkins University. He studied first aniline, monoalkyl anilines and dialkyl anilines. The values between 2.7 and 3.4 μ appear to be of considerable interest and perhaps value in distinguishing primary, secondary and tertiary amines. Upon continuation of his study [33] of the amines the values for certain alkyl and aryl naphthylamines were determined,[34] the values of di- and triphenylamines, and finally those for mono-, di- and tribenzylamines.[35] The same qualitative differences were observed at 3.3 μ between the primary, secondary and tertiary amines in each of the series investigated. The values from alpha and beta naphthylamine were similar. Bell [36] has also studied naphthalene and benzene.

At the Color Laboratory of the Bureau of Chemistry Berliner and May [37] have studied the vapor pressures of various nitroanilines and have determined the latent heat of vaporization and entropies. This is apparently the first of a series of papers to obtain accurate vapor pressure determinations of many organic compounds.

A determination of hydrogen ion concentration by spectrophotometric methods has received much stimulus in the past few years through the original work of Brode at the University of Illinois and later at the Bureau of Standards, and by Holmes and his associates at the Bureau of Chemistry. Holmes and Snyder [38] have determined the ionization of 1-naphthol-2-sodiumsulfonate indophenol. Holmes [39] has extended the spectrophotometric work to identification of many dyes. French [40] has

[32] J. Am. Chem. Soc., **47**: 2192; 1925.
[33] J. Am. Chem. Soc., **47**: 3039; 1925.
[34] J. Am. Chem. Soc., **48**: 813; 1926.
[35] J. Am. Chem. Soc., **48**: 818; 1926.
[36] J. Am. Chem. Soc., **47**: 2811; 1925.
[37] J. Am. Chem. Soc., **47**: 2350; 1925.
[38] J. Am. Chem. Soc., **47**: 2232; 1925.
[39] Ind. Eng. Chem., **17**: 918; 1926.
[40] Ind. Eng. Chem., **18**: 298; 1926.

shown that concentration of the dye solution has an importan effect on the value of the extinction coefficient of methylene blue

Smythe [41] of Princeton University has continued his work o the electric moments of various molecules. Assuming that th structures of various organic compounds are formed by the link age of atoms by electron pairs symmetrically located at the apice of regular tetrahedrons, he has calculated values for the electri moments and has found that they agree surprisingly well wit the experimental values. The particular paper referred to de scribes work on aromatic acids and esters.

Francis, Hill and Johnston [42] have started a careful study o the directive influence on substitution in the benzene ring, de termining first the rates of bromination of many ortho, met and para isomers particularly amino and hydroxy compounds i acid solution and also the relative rates in successive steps o bromination. This work has been continued by Francis [43] a the Massachusetts Institute of Technology, who discusses th mechanism of bromination in aqueous solution and concludes tha it is not due to hypobromous acid as is usually assumed, but t nascent bromine. A second paper [44] describes the partial bromina tion of many derivatives of aniline giving competition experi ments. Francis, Andrews and Johnston [45] have pointed out th parallelism between the relative effect of the presence of a grou in an aromatic compound upon its melting and boiling tempera ture and heat of melting on the one hand and the directiv influence of the group on the other, and finally Francis [46] ha offered a large number of additional experiments extending th work of the first paper in this series.

In the field of dyes and dye intermediates, Quayle and Reid [4 of Johns Hopkins University have described a large number o fluorine, chlorine and alkyl derivatives of benzoyl-*o*-benzoic aci and the corresponding anthraquinones, and Palmer and Reid [4 have discussed the effect of sulfur and sulfone groups upon th color of certain azo dyes. Beisler and Bray [49] have describe the preparation of 1-benzoylamino-2-methylanthraquinone; Reyn

[41] J. Am. Chem. Soc., **47**: 1894; 1925.
[42] J. Am. Chem. Soc., **47**: 2211; 1925.
[43] J. Am. Chem. Soc., **47**: 2340; 1925.
[44] J. Am. Chem. Soc., **47**: 2588; 1925.
[45] J. Am. Chem. Soc., **48**: 1624; 1926.
[46] J. Am. Chem. Soc., **48**: 1631; 1926.
[47] J. Am. Chem. Soc., **47**: 2357; 1925.
[48] J. Am. Chem. Soc., **48**: 528; 1926.
[49] J. Am. Chem. Soc., **47**: 2371; 1925.

olds and Bigelow [50] of Brown University the details for the preparation of quinizarin; Philips and Goss [51] at the Bureau of Chemistry, the preparation of methylisopropyl quinoline yellow; Bogert and Evans [52] of Columbia University, new dye intermediates formed by condensing 2, 4-dinitrochlorobenzene with sodium salts of phenol and thiophenol; Lewis and Lowy [53] of the University of Pittsburgh, a comparison of azo dyes from H and acetyl H acid.

A few of the new methods or modifications of old methods of preparation of certain aromatic compounds are worthy of mention. Gomberg and Pernert [54] have described the preparation of a number of methylbiphenyl compounds by diazotizing toluidine and coupling with benzene. Houston and Johnson [55] have advocated the use of nitrogen tetroxide in anhydrous benzene for diazotizing aromatic amines. Examples are given with the nitroanilines.

Fry and Grote [56] have made a study of the effect of conditions and substituents upon the Sandmeyer reaction. Hurd [57] at Northwestern University has shown that ketenes react with certain types of organic compounds to give acetyl derivatives. Although complex mixtures were obtained on account of the great reactivity of the ketene, nevertheless, under proper conditions, ketene may offer interesting possibilities as an acetylating agent, particularly since ketene is so readily prepared from acetone.

At the University of Minnesota the general study of the decomposition of halogenated phenols and their salts has been continued. Hunter and Levine [58] have described the oxidation of bromo and chloro derivatives of 1,3-pyrogallol dimethyl ether to mono- and di-molecular products of known constitution, the formation of which can readily be explained through the assumption of univalent oxygen radicals. Hunter and Morse [59] have carried out similar work with trichlorophenols with analogous results, and Lauer [60] has given a further discussion of the structure of tribromophenol bromide. Smith and Dobrovolny [61] from the same

[50] J. Am. Chem. Soc., **48**: 420; 1926.
[51] J. Am. Chem. Soc., **48**: 823; 1926.
[52] Ind. Eng. Chem., **18**: 1299; 1926.
[53] Ind. Eng. Chem., **18**: 1289; 1926.
[54] J. Am. Chem. Soc., **48**: 1372; 1926.
[55] J. Am. Chem. Soc., **47**: 3011; 1925.
[56] J. Am. Chem. Soc., **47**: 710; 1925.
[57] J. Am. Chem. Soc., **47**: 2777; 1925.
[58] J. Am. Chem. Soc., **48**: 1608; 1926.
[59] J. Am. Chem. Soc., **48**: 1615; 1926.
[60] J. Am. Chem. Soc., **48**: 442; 1926.
[61] J. Am. Chem. Soc., **48**: 1693; 1926.

laboratory have described some peculiar compounds which are formed from duroquinone and sodium malonic ester.

At the University of Iowa, Raiford and his associates have extended their general studies of acylated *o*-aminophenols and their rearrangement products to a study of 4-amino-4¹-hydroxydiphenyl and 2, 7-disubstituted naphthalene. In no case did Raiford and Clark [62] find rearrangement to take place which might indicate the proximity of the substituting groups in these compounds. Acylation of *o*-aminophenols is also being studied at Purdue University by Nelson and Davis [63] and Nelson and Aitkenhead.[64]

At Princeton University, Jones and his associates are continuing the study of amine oxides and hydroxylamines. Jones and Wallis [65] studied the rearrangement products of certain hydroxamic acids and acid azides containing an optically active group. Optically active products were obtained. Jones and Root [66] have attempted the rearrangement of certain hydroxamic acids isomeric with triphenylacethydroxamic acid, but since no rearrangement occurred the conclusion was drawn that the character of the triphenylmethyl group is the essential consideration and not the weight.

Orndorff and his associates, Schade, Cornwell, Gibbs, and Shapiro,[67] at Cornell University have continued their study of the preparation of numerous phthaleins, sulfophthaleins and their derivatives.

A few individual papers of interest have appeared. Butler and Adams [68] of the University of Illinois have made a study of diaminodiphenyl methane derivatives and have demonstrated that the peculiar isomerism existing in the diphenyl series does not exist in the diphenyl methane series. Jacobson and Adams [69] have continued the work on the preparation of polyhydroxy anthraquinones and have clarified the orientation which takes place in the synthesis of these compounds from opianic acid in condensation with various phenols and phenol ethers.

Gomberg and Anderson [70] of the University of Michigan have

[62] J. Am. Chem. Soc., **48**: 483; 1926.
[63] J. Am. Chem. Soc., **48**: 1677; 1926.
[64] J. Am. Chem. Soc., **48**: 1680; 1926.
[65] J. Am. Chem. Soc., **48**: 169; 1926.
[66] J. Am. Chem. Soc., **48**: 181; 1926.
[67] J. Am. Chem. Soc., **48**: 769, 981, 1327; 1926.
[68] J. Am. Chem. Soc., **47**: 2610; 1925.
[69] J. Am. Chem. Soc., **47**: 2011; 1925.
[70] J. Am. Chem. Soc., **47**: 2022; 1925.

made a very careful study of the structure of *o*-cresaurin and triphenylros-*o*-toluidine.

Fuson [71] at Harvard University has made a study of certain quinoline derivatives, from which he concludes that the centroid structure for the quinoline nucleus is unwarranted.

[71] J. Am. Chem. Soc., **47**: 2018; 1925.

Chapter XVII.

Heterocyclic Organic Chemistry.

Treat B. Johnson,

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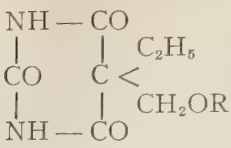
Listed below are the names of the universities and colleges, research institutes and industrial laboratories in the United States where research work in heterocyclic chemistry was carried on this past year, and original contributions were made to our knowledge of the chemistry of this type of organic substances. In the table, which follows, are also recorded the types or classes of cyclic organic combinations investigated, and the names of the various co-workers who coöperated in the respective investigations. It is quite apparent from the data recorded in the table that the study of organic ring systems has been a prominent feature of American research in organic chemistry this past year. When one considers the large number of ring systems theoretically capable of existence according to our accepted theory of organic structure, and the enormous number and complexity of new substances which are possible of synthesis, he is forced to conclude that this branch of organic chemistry, if properly cultivated, offers probably greater possibilities for discovering new organic combinations of scientific interest and practical utility than any other field of organic chemistry. We have hardly penetrated today through the outside defenses of a new world of chemical compounds.

Several of our American investigators are active in developing the chemistry of the barbituric acid group of compounds. These combinations have a double interest on account of their possible therapeutic application. Hill and Keach [1] have devoted

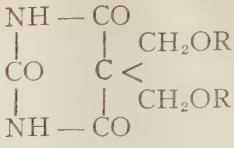
[1] J. Am. Chem. Soc., 48: 257, 1926.

Universities and Colleges	Types of Organic Compounds Studied	Investigators
University of Buffalo.	Pyridones	C. R. Reigel, N. C. Reinhard
Columbia University.	Benzo-thiazoles	M. T. Bogert, A. Stull, H. B. Corbitt
University of California	Quinolines	R. C. Fuson
University of Chicago	Methylene blue	T. Chalkley, Jr.
Harvard University..	Oxazines, iso-ozaxolines, isoxazoles	E. P. Kohler, G. R. Barrett
University of Indiana	Hexamethylenetetramine	G. C. Hale
University of Kansas	Thiazolidines	F. B. Dains, R. E. Brewster, I. Malm, A. W. Miller, R. V. Mansval, J. A. Sultzaberger
University of Louisville	Acridines	A. W. Homberger, H. Jensen
Mt. Holyoke College.	Polypeptide-hydantoins	D. A. Hahn, E. Gilman, E. P. Carr, M. A. Dobbrow
University of Michigan	Acridines (acridyl radicals)	M. Gomberg, D. L. Tabern
Geo. Washington University	Thiazolidines	R. M. Hahn
Yale University	Pyrimidines, purines, glyoxalines	T. B. Johnson, A. J. Hill, E. Gatewood, R. D. Coghill, E. W. Rugeley, D. F. Keach
Research Institutes		
Mellon Institute	Pyrimidines (barbituric acids)	L. H. Cretcher, J. A. Koch, W. H. Pittenger
Mayo Foundation ...	Indoles	E. C. Kendall, A. E. Osterberg, B. F. Mackenzie
Rockefeller Institute.	Nucleosides (purines and pyrimidines)	P. A. Levene, H. Sobotka
Industrial Laboratories		
Abbott Laboratory ..	Pyrimidines (barbituric acids)	E. H. Volweiler

much attention to the study of ether combinations of types I and II, but up to the present time they have not discovered any substance in these two series which has exhibited a favorable therapeutic action. Of these new barbituric acid derivatives but



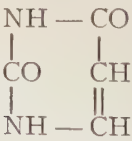
I



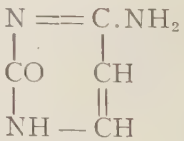
II

one, namely, ethyl benzyloxymethyl barbituric acid, possesses a notable hypnotic effect. This property, however, is unfortunately offset by an objectionable toxicity which renders it valueless for medicinal practice. Pharmacological tests are now in progress on several of these new compounds. Volweiler [2] has compared the hypnotic activity and toxicity of certain members of the barbituric acid series in which one of the alkyl groups is replaced by an allyl group. He reports that the replacement of an alkyl group in 5,5-dialkylbarbituric acids by an allyl group frequently leads to an increase in toxicity. Cretcher, Koch and Pittenger [3] add to our knowledge of the barbituric acid series by synthesizing various combinations in which an alkyl group is replaced by different β-hydroxyalkyl groups. The parent substance of their series was originally synthesized by Johnson and Shepard.[4] The results of the study of the pharmacology of these substances has not been reported.

In their researches on the chemistry of bacteria Johnson and Coghill [5] have made the interesting discovery that 5-methylcytosine (VI) is present among the hydrolytic products of tuberculinic acid, the nucleic acid occurring in *Tubercle bacilli*. This amino pyrimidine has the same structural relationship to thymine V as exists between uracil III and cytosine IV. It was first synthesized by Wheeler and Johnson.[6]

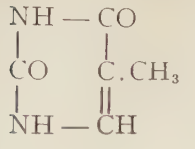


III
(Uracil)

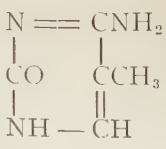


IV
(Cytosine)

[2] J. Am. Chem. Soc., 47: 2236; 1925.
[3] J. Am. Chem. Soc., 47: 3083; 1925.
[4] J. Am. Chem. Soc., 35: 1003; 1913.
[5] J. Am. Chem. Soc., 47: 2838; 1925.
[6] Am. Chem. J., 31: 591; 1904.

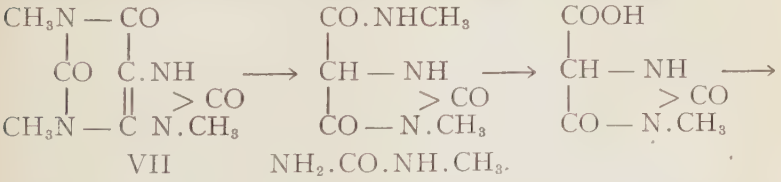


V
(Thymine)



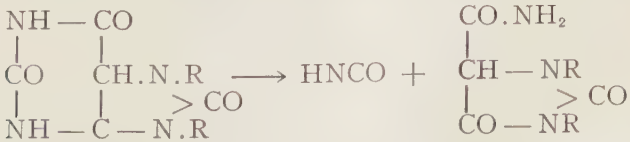
VI
(5-Methylcytosine)

Important contributions to purine chemistry are two papers by Miss Gatewood,[7] in which are reported the influence of alkali on substituted uric acids of the following constitutions: 1, 3, 7-trimethyl-9-phenyluric acid, 1, 3, 7, 9-tetramethyluric acid and 1, 3, 9-trimethyluric acid. The first paper of her series was published in 1923.[8] The varying stability of substituted uric acids towards alkali is discussed critically in this work, and a careful study of the mechanism of alkali decomposition has been made. All these acids are characterized by their property of losing their purine structure and being transformed by the action of alkali into hydantoin compounds or their decomposition products. The different stages of molecular decomposition of 1, 3, 9-trimethyluric acid (VII), for example, may be expressed as follows:



VII $NH_2.CO.NH.CH_3$.

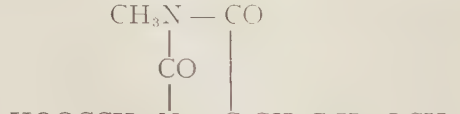
In other words, the same type of amide derivatives of hydantoin are formed by the action of alkali on these acids as is obtained by Biltz and his co-workers by thermal decomposition of hydroxydihydrouric acids (VIII).[9]



VIII

[7] J. Am. Chem. Soc., **47**: 2175, 2181; 1925.
[8] J. Am. Chem. Soc., **45**: 3056; 1923.
[9] Biltz and Lachmann, J. prakt. Chem., 113: 309; 1926.

Work in the field of polypeptide-hydantoins has been in progress in the Mt. Holyoke laboratory, and three papers of unusual interest have been published during the year by Hahn and Gilman [10] and Carr and Dobbrow.[11] These cyclic combinations are of scientific interest on account of their possible structural relationship to proteins. The most interesting result reported, from a purely structural point of view, is the discovery that hydantoin compounds represented by Formula IX are especially characterized by their ability to occur in geometrical modifications. The lower melting isomers are apparently unstable in alcoholic solution acidified with hydrochloric acid and are transformed almost quantitatively under such conditions into the higher melting or stable modifications. A physico-chemical study of various unsaturated hydantoin combinations has revealed the fact that meas-



IX

urements of ultra-violet absorption spectra are very helpful in the final settlement of constitution in this series. Hydantoins substituted on nitrogen atoms in positions 1 and 3 of the hydantoin ring are characterized by their own specific absorption spectra and Carr and Dobbrow have given another illustration of the practicability of this method of research and its utility in determining organic structure.

It was hoped that ethyl γ, γ-diethoxyacetoacetate (X) would prove to be a useful reagent as the starting point for the synthesis of glyoxaline combinations. Rugeley and Johnson [12] attempted to use it for this purpose, especially the development of a new synthesis of glyoxal propionic acid (XI), thereby making available β *glyoxaline propionic acid* (XII) from a new source. While they were successful in accomplishing the object desired the method is of no practical value for synthesis on account of the poor yield obtained.

[10] J. Am. Chem. Soc., 47: 2941, 2953; 1925.
[11] J. Am. Chem. Soc., 47: 2961; 1925.
[12] J. Am. Chem. Soc., 47: 2995; 1926.

$(C_2H_5O)_2CH.CO.CH_2COOC_2H_5$

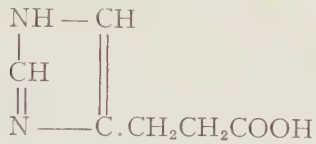
X

$(C_2H_5O)_2CH.CO.CHCOOC_2H_5$

$CH_2COOC_2H_5$

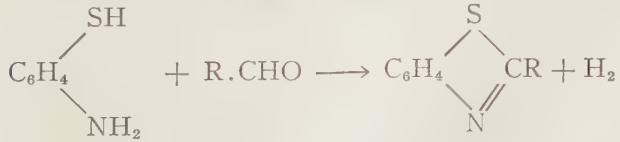
$OCH.CO.CH_2.CH_2.COOH$

XI



XII

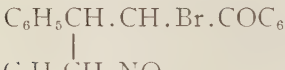
Contributions continue to be made to our knowledge of the chemistry of thiazoles by Bogert and his co-workers,[13] three papers having been published this past year. Their work is confined to the study of benzothiazole combinations. These researches have been undertaken with the belief that there existed the possibility of discovering in this field new products of therapeutic interest. Various combinations have been made from *o*-aminophenyl mercaptan and its disulfide which has been recommended by McDonagh [14] under the name Intramine for use in the treatment of spirochetal infections. Thus far no outstanding therapeutic properties have been revealed among the various derivatives prepared. In contradiction to the statement of Claasz [15] that *o*-aminophenyl mercaptan condenses with aldehydes to form thiazolines, these workers find that the condensation reaction does not lead to these products but to true thiazoles as originally stated by Hoffmann.[16] Dains and his co-workers [16a]



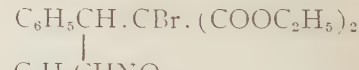
[13] Bogert and Stull, J. Am. Chem. Soc., 47: 3078; 1925. 48: 248; 1926. Bogert and Corbitt, 48: 783; 1926.
[14] Lancet, 190: 238; 1916. German Pat. 68,697; 1892.
[15] Ber., 45: 1031; 1912. 49: 1141; 1916.
[16] Ber., 13: 1236; 1880.
[16a] J. Am. Chem. Soc., 47: 1981; 1925.

have also added to our knowledge of thiazoles; having continued their general study of the action of alkylene bromides upon disubstituted thioureas RNHCSNHR′ where the groups R and R′ are different with the purpose of ascertaining the effect of these different groups upon the constitution of the resulting thiazolidines. Although the experimental work reveals a tendency to selective action when the groups R and R′ are altered, no general rule can be stated, however, which enables one to predict beforehand the structure of the cycle formed in a given reaction. Hahn [17] has simply made new applications of a quite general reaction of thiazolidones containing a reactive methylene grouping in the $-CO.CH_2.S-$ linkage and applied several new condensations reactions with a series of aldehydes of the vanillin type.

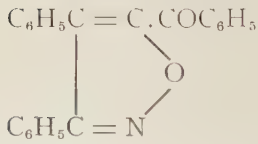
Kohler [18] continues to add to our knowledge of the chemistry of ring compounds containing oxygen, nitrogen and carbon in the cycle, and contributes two more papers to his series on the chemistry of isoxazolines. The work discussed has no biochemical significance and possesses scientific interest only. The work discussed in these two papers has been developed from a study of reactions characteristic of nitro-halogen compounds represented, for example, by Formulas XIII and XIV. Compounds



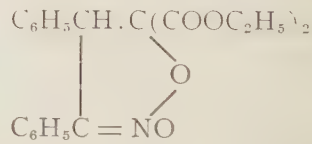
XIII



XIV



XV

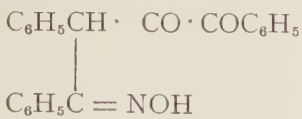


XVI

of this type are easily transformed into the corresponding cyclic combinations-isoxazolines represented by Formulas XV and XVI respectively. The peculiar sensitiveness of such compounds and the many possibilities for isomerization of certain ketone-oxime combinations brought into the research has called for very careful chemical reasoning and good laboratory technic, in order to arrive at the correct solution of the constitution of various com-

[17] J. Am. Chem. Soc., 47: 1998; 1925.
[18] J. Am. Chem. Soc., 47: 3030; 1925. 48: 1770; 1926.

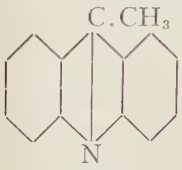
pounds obtained in the research. Isoxazolines of the type represented by Formula XVI resemble in their chemical behavior amine oxides. Not only can oximes like that represented by Formula XVII be isomerized to isoxazolines, but also transformed under specific experimental conditions into true orthoxazine compounds of which very few derivatives are actually known.[19]



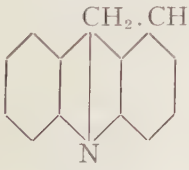
XVII

Brief mention only will be made of two papers dealing with certain phases of the chemistry of acridine compounds. Gomberg and Tabern[20] bring forward new experimental evidence to support the theory previously advanced from their laboratory that triarylmethyls possess the property of selective absorption in the visible spectrum, not merely because of the trivalent carbon atom in them, but rather in virtue of the quinoidation of the free radical. The complex free radicals—acridyls—have been incorporated into their study of the interesting phenomena of such unstable combinations, and from the observations made they conclude that in the acridyls, in common with other free radicals, the acquisition of the property of selective absorption on the one hand, and on the other, their capacity to exist tautomerically in the quinonoid state, are concomitant phenomena.

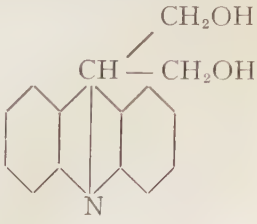
Homberg and Jensen[21] call attention to the fact that the methyl group in 9-methylacridine (XVIII) cannot be oxidized to acridine-9-carboxylic acid. The group does, however, interact smoothly with formaldehyde giving a mixture of the two alcohol derivatives represented by Formulas XIX and XX. Both of



XVIII



XIX

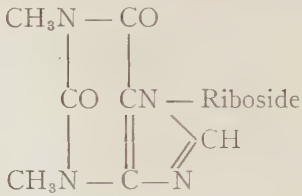


XX

[19] J. Am. Chem. Soc., **48**: 754; 1926.
[20] J. Am. Chem. Soc., **48**: 1345; 1926.
[21] J. Am. Chem. Soc., **48**: 800; 1926.

these compounds are oxidized easily to the desired 9-acridine-carboxylic acid by the action of potassium dichromate.

Levene has continued to add to the literature new facts contributing to a better understanding of the structure of purine and pyrimidine cycles. Working with Sobotka[22] he has succeeded in coupling the sugars xyloside and riboside with theophylline and found that the riboside combination is identical with dimethyl xanthosine which has previously been obtained from guanosine. The structure of the nucleoside is represented by Formula XXI. For the preparation of pyrimidine nucleosides



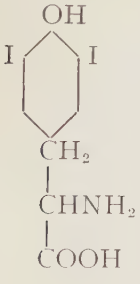
XXI

further attempts were made to obtain natural glucosidic combinations by the action of acetobromoglucose on the alkali and silver salts of pyrimidines belonging to the uracil series.[23] Quite in accordance with the observations of other investigators they found that this procedure did not permit of the smooth synthesis of such combinations. In other words, no good method is yet available for the synthesis of pyrimidine nucleosides.

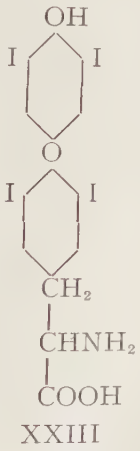
The last paper to which I shall refer in this report is the contribution of Kendall, Osterberg and MacKenzie[24] on the subject of indoles. These investigators have previously reported that the results of ultimate analysis and the chemical properties of the thyroxine molecule indicate that the correct formula to be assigned to this iodine compound is 4,5,6-triiodo-2-oxo-2,4,5,6-tetrahydroindole-3-propionic acid. Accepting this conclusion as securely established they, therefore, decided to prepare a series of indole compounds closely related to the thyroxine structure and endeavor to prove the correctness of their hypothetical formula. In this paper they give a description of the synthesis of 2-oxodihydro- and 2-oxohexahydro-indole-3-propionic acids. Their method of synthesis has involved the application of fundamental reactions of considerable interest, but assignments of

[22] J. Biol. Chem., 65: 463; 1925.
[23] J. Biol. Chem., 65: 469; 1925.
[24] J. Am. Chem. Soc., 48: 1384; 1926.

certain constitutional formulas to some of the compounds described by them will, no doubt, lead to a discordance of opinion as to their correctness among organic workers who have had experience in the investigation of heterocyclic combinations. The authors give data only concerning the properties of their key compounds, and state that a full discussion of the structural formulas proposed is reserved for a later publication. Their new combinations will very probably be found to possess unique and pronounced biological activity. In the light, however, of important developments which have taken place since the publication of this interesting paper, it can now be concluded that the specific biological action of thyroxine is not to be accounted for by the indole constitution. The compounds prepared possess only biological interest in so far as the question of thyroxine is concerned. Harrington [25] has recently shown that the thyroxine molecule is not constructed on an indole nucleus, but is an aromatic combination related in structure to the amino acid tyrosine and very probably is to be assigned the constitution represented by Formula XXIII. When the iodine atoms are replaced by hydrogen the mother substance represented by Formula XXIV is produced. This compound has been synthesized by Harrington and shown to be identical with reduced thyroxine. Thyroxine is therefore an iodo-substituted phenylether derivative of diiodotyrosine XXII, which is found in nature.



XXII



XXIII

XXIV

[25] Biochem. J., 20: 300; 1926.

Research Problems.

In this addendum are recorded some suggestions for new research in the field of heterocyclic chemistry with the hope that some young researcher will be helped in the selection of a chemical problem in organic chemistry for his personal investigation. Only a limited number of problems for research are given. Others will be suggested in each publication of this year-book.

1. Utilization of acetylene for the commercial preparation of thiophene and pyrrole compounds by interaction of this unsaturated hydrocarbon with sulfur and ammonia.

2. Furfural is now an organic product which can be produced in commercial quantities. The further development of the chemistry of this compounds offers a rich field for investigation.

3. New applications of sodium azide (NaN_3) for organic synthesis is desirable. This salt is now available as a specific reagent for scientific investigation.

4. New methods and improved technic for synthesizing pyrrole compounds. A practical commercial method of manufacturing pyrrole would stimulate research in this field. Our knowledge of the chemistry of blood and plant pigments would be advanced if we knew more about the fundamental chemistry of pyrroles.

5. It is important to develop further the chemistry of cyclic combinations containing sulfur. Not only does the thiophene series offer work of scientific and practical interest, but the dithiene compounds or the sulfur analogues of piperazine need to be studied. The study of sulfur compounds from a biochemical standpoint has taken on a renewed interest since the discovery of glutathione and insulin. A better knowledge of the chemistry of sulfur combinations will also be helpful in the study of petroleum products containing sulfur.

6. What is greatly needed to stimulate new research in nitrogen chemistry is some practical method of activating nitrogen. Nitrogen in heterocyclic organic combinations is a very reactive element; in the molecular condition it is very inert.

Chapter XVIII.

Azo Dyes and Intermediates.

E. F. Hitch,

Chief, Azo Dyes Division, Jackson Laboratory,
E. I. duPont de Nemours & Company.

With the possible exception of indigo and sulphur black, azo dyes represent the largest single class of synthetic coloring matters from the standpoint of quantity produced and variety of shade. This is due to the fact that an almost infinite number of dyes can be made from the intermediates now available, to the relative cheapness and ease of application of this class of colors, and to their universal application. They may be employed for the dyeing of all textile fibers, such as cotton, wool, silk, paper, linen, viscose and acetate silk, as pigments in the paint and varnish industry, as food colors, for the manufacture of printing inks, for coloring oils, fats and waxes, and for dyeing leather.

The progress in the chemistry and chemical technology of azo dyes over any given period is shown by the amount of theoretical work done in this field as evidenced by publications of the results of such investigations, by the number of new colors placed on the market by the manufacturers, by the improvements in quality and dyeing properties of the old dyes, by economies in manufacturing operations as shown by price reductions, and by the number of patents issued in this field.

It is very encouraging to note that some research work on azo dyes has been done during this period by our universities and colleges. The Bureau of Standards and the Color Laboratory of the Bureau of Chemistry in Washington have also contributed to the advancement of knowledge in this field. The fact that some investigation work is being done by the university and government laboratories indicates that we may expect in the future a closer coöperation between the industries and those engaged

in purely theoretical work. This is indeed an encouraging sign of progress. Mention should be made of the work done by A. S. Wheeler and his co-workers [1] at the University of North Carolina on the halogenated amino-*p*-xylene and halogen amino-*p*-cymene and the azo dyes obtained therefrom, and of the work of Palmer and Reid [2] at Johns Hopkins University on the influence of sulfur on the color of azo dyes and of Lewers and Lowy [3] at the University of Pittsburgh on azo dyes from H-acid and acetyl H-acid. Some interesting spectrophotometric work on dyes is being done at the Bureau of Standards.[4] Those interested in the identification of azo dyes will find valuable information in the work of W. C. Holmes at the Color Laboratory of the Bureau of Chemistry on the reduction products of azo dyes, now being published in The American Dyestuff Reporter.

During this period about forty new azo colors were announced by the dyestuff manufacturers of this country. It is estimated that about ten of these colors are really new in the sense that these dyes as chemical individuals had not previously been placed on the market. These ten distinctly new colors represent the result of original investigation in the research laboratories of the industry. The fact that these new and original dyes developed by American chemists have been manufactured successfully is a very hopeful sign of progress. The permanent success of the dye industry in this country depends upon the research chemist, and upon his ability to discover new and valuable dyes. The older dyes are gradually being replaced by colors having better fastness properties or by those which are more suitable for the variety of fibers now in use by the textile industry. The advent of these new dyes indicates a healthy growth of the American industry, and is an attempt on the part of our dye manufacturers to meet the increasing demand for faster colors. The remaining thirty azo colors which were placed on the market during this period represent some of the older and well known colors which have been made for the first time by American manufacturers, and some of the older colors which have been improved in quality. At the present time the American manufacturers of azo dyes are in a position to supply to the dyer all of the desirable pre-war colors, many of these being

[1] J. Am. Chem. Soc., **47**: 178; 1925.
[2] J. Am. Chem. Soc., **48**: 528; 1926.
[3] Ind. Eng. Chem., **17**: 1289; 1925.
[4] Ind. Eng. Chem., **18**: 627, 708; 1926. J. Am. Chem. Soc., **48**: 1984; 1926.

distinct improvements over the pre-war types. In addition, our industry has perfected distinctly new and superior colors, which are the products of research in our industrial laboratories. This is a remarkable achievement. The magnitude of the task can be realized when it is understood that, in the short period of ten years, processes for the manufacture of hundreds of colors have been developed in the laboratory and carried through to successful operation on a plant scale—each color requiring special care and accurate control of the many steps in the process of manufacture. In addition to this the intermediates used in the manufacture of these colors must be of the proper quality. It was therefore necessary to develop methods for the manufacture of a hundred or more intermediates. All this has been accomplished, and more. The achievements of the past year in the production of new azo colors shows beyond a doubt that the American manufacturers are in the industry to stay; that they have reached a point where they are no longer willing to follow in the footsteps of others, but have determined to be pioneers in this field. So long as this attitude is maintained the success of the industry is assured.

One of the most remarkable achievements in azo dye manufacture during this period is in economy of operation. Competition has been so keen that reductions in cost obtained by increased yields and more efficient operations have been passed on very rapidly to the consumer. The reduction in selling prices of these dyes is therefore a very accurate measure of operation economy. As pointed out by Irenée duPont [5] in an address before the American Chemical Society at its last meeting in Philadelphia the selling price of American dyes, based on the present value of the dollar, closely approximates the pre-war level. This indicates that intensive research work has been done in the laboratories of the dye manufacturers, with the result that material increases in yields and economies of operation have been obtained.

Six U. S. Patents on azo dyes have been granted during this period to Americans or assigned to American firms. U. S. P. 1,547,526 covers the preparation of monoazo dyes by the condensation of nitrosocarbazol disulfonic acid with aromatic amines. U. S. P. 1,549,214 covers tetrakisazo dyes obtained from the urea of J-acid. U. S. P. 1,557,265 claims azo dyes suitable

[5] Ind. Eng. Chem., 18: 1002; 1926.

for coloring oils, waxes, rubber, lacquers, etc., formed from the aminoazoxylenes and β-hydroxynaphthoic acid. The dyes described in U. S. P. 1,572,417 are not azo dyes but the basic compound is formed by a curious reaction of diazonium compounds. For example, benzene diazonium chloride is caused to react with *m*-phenylenediamine at 90° C. whereby the quinone hydrochloride of aminodiphenylamine is formed. This is used as a base, or chromogen, for the formation of a number of dyes by condensation with compounds such as sodium methylate, sodium salicylate, *p*-hydroxyphenylglycocoll, potassium cyanide, etc. U. S. P. 1,586,693 covers the monoazo dyes formed by combining aminodiphenylamine sulfonic acid and its derivatives with acetyl H-acid. U. S. P. 1,589,936 describes a process for the reduction of azo compounds to hydrazo compounds. Eighteen patents have been issued covering the intermediates for azo colors. All but one of these deal with the process of manufacture of intermediates. U. S. P. 1,574,337 covers the product 2, 4-diaminodiphenyl ether.

A very important and relatively new field of dye chemistry has shown but little advancement in this country. This is the line of the so-called "Naphthols." These compounds are derivatives of β-hydroxynaphthoic acid, formed by condensation of this acid with primary aromatic amines. The naphthols are applied directly to the fiber and the color is developed by coupling with a diazo compound. For the convenience of the dyer the diazo compound is frequently supplied by the manufacturer in the form of a dry stabilized salt. The "Rapid Fast Colors" are mixtures of the nitrosamines from diazo compounds and the naphthols. They can be applied in a manner similar to direct colors. These dyes, when formed from compounds not containing sulfonic acid groups, are extremely fast to washing and of good fastness to light. Because of the increasing demand for fast colors these products are being more extensively used.

For continued advancement in the field of azo dyes from a commercial standpoint there is needed a type of colors having the ease of application characteristic of these dyes with fastness properties comparable with the vat colors. We believe such a goal is not impossible of attainment.

Of the many problems for fundamental research in this field the most important appears to be an intensive study of the relation of structure of azo dyes to their fastness properties. A

more specific problem of vital interest to the manufacturer is a determination of the reactivity of the diazonium group in the formation of azo compounds. The investigation of such problems would be very interesting and fruitful research for our universities. The pursuit of such fundamental research is certain to lead to important discoveries. Such discoveries may revolutionize our ideas of color and color manufacture.

Chapter XIX.

Vat Dyes and Intermediates.

Elmer K. Bolton,

Director Chemical Section, Dyestuffs Department,
E. I. duPont de Nemours & Company.

The vat dyes are divided chemically into three well defined classes. The first of these, the indigoid group, owe their name to their chemical relationship to indigo. The second group, the anthraquinone vat dyes, are derived from anthraquinone. The third group, the hydron blues, are made from carbazol. The fields of indigoid and anthraquinone vat dyes, because of their excellent fastness properties, have been investigated extensively in the past and this activity has continued during the period to be reviewed. The work for the most part has been carried out in the research laboratories of the companies offering these lines of colors and only a few investigations in the field of anthraquinone derivatives have been undertaken in the laboratories of our universities. The research activities of American companies have been confined very largely to improvements in the quality and yields of colors already marketed, and intermediates from which they are derived, and to the development of processes for the manufacture of products that have been imported in appreciable quantities but have not previously been made in this country. As a result of continued research work on products already on the American market, improvements in manufacturing costs have been realized and have been passed on to the consumer. An example of the progress that has been made in the reduction of selling prices is illustrated by a comparison of the selling price of indigo 20% paste with pre-war figures. In 1913 and 1914 this dye was sold at 15½¢ per pound, whereas the American selling price in 1925 was 14¢. Considering the

purchasing power of the dollar as 59¢ for 1925, the selling price of 14¢ is equivalent to 8¼¢ in 1914.[1]

During the year ending July 1st, 1926, the following vat dyes have been made for the first time in America and are equal in every respect to their German prototypes.

Anthrene Black DS (Newport)
Anthrene Scarlet 2G (Newport)
Anthrene Red BN (Newport)
Ponsol Red Violet RRNX (duPont)
Ponsol Red BN (duPont)
Ponsol Pink B (duPont)
Sulfanthrene Violet B (duPont)
Thianthrene Pink FB (Newport)

In reviewing the research activities of our universities we find that Jacobson with Adams [2] has prepared polyhydroxy and polyhydroxymethylanthraquinones by condensing opianic acid (3, 4-dimethoxy-2-carboxybenzaldehyde) with para-substituted phenols to give substituted phthalides which can be reduced to the benzylbenzoic acids. These intermediates have been converted to anthrones and finally to anthraquinones. A number of new anthraquinones have been prepared by this general method.

Quayle and Reid [3] have prepared substituted *o*-benzoylbenzoic acids and their corresponding anthraquinones by condensing phthalic anhydride with fluorotoluene, fluoro- and chloroethylbenzenes, diethyl-, diisopropyl, and cyclohexylbenzenes. The resulting *o*-benzoylbenzoic acids have been condensed to the corresponding substituted anthraquinones.

Phillips [4] of the Color Laboratory has described the preparation of 2-amino-anthraquinone from phthalic anhydride and chlorobenzene and has determined the effect of time, temperature, amount of ammonia, and catalyst upon the quality and yield of the beta-amino-anthraquinone.

Rhodes, Nichols and Morse [5] have studied the Hoechst test for the determination of anthracene and have modified this method so that it is more accurate and more rapid than the standard test.

Beisler and Bray,[6] have described the preparation and prop-

[1] Ind. Eng. Chem., 18: 1002; 1926.
[2] J. Am. Chem. Soc., 47: 2011; 1925.
[3] J. Am. Chem. Soc., 47: 2357; 1925.
[4] Ind. Eng. Chem., 17: 721; 1925.
[5] Ind. Eng. Chem., 17: 839; 1925.
[6] J. Am. Chem. Soc., 47: 2371; 1925.

erties of 1-benzoylamino-2-methylanthraquinone by condensing 1-amino-2-methylanthraquinone with benzoyl chloride.

In the field of indigoids there has been considerable activity at home and abroad, particularly in the discovery of new colors of this series. An improvement in controlling the fusion of phenylglycine to indoxyl has been described by the Dow Chemical Co.;[7] this consists in mixing phenylglycine with a hydrocarbon like kerosene which forms a blanket medium for the melt protecting the fusion mixture and facilitating the mixing of the phenylglycine with caustic alkali.

A new process for making indigo by the oxidation of aniline in acid solution has been described by Gupta.[8]

New thionaphthisatins have been obtained by condensing thionaphthols which have no free alpha-position in ortho-position to the SH-group with oxalyl chloride (Society of Chemical Industry).[9]

Joyce[10] of the Chemical Foundation has prepared arylthioglycollic acids, specifically 5-chloro-3-methylphenylglycollic acid, by diazotizing an *o*-aminoarylthioglycollic acid, then adding alcohol and reducing with iron and sulfuric acid.

New violet vat dyes have been obtained by the duPont Company[11] by condensing halogenisatin chloride with hydroxymethyl-halogen-thionaphthene. As an example, dibromoisatin chloride is condensed with 2-hydroxy-3-methyl-5-chlorothionaphthene.

Violet dyes of the 2-thionaphthene-2-indolindigo series have been described by Grasselli Dyestuff Corp.;[12] they are prepared by condensing, as an example, dibromoisatin chloride with 5, 7-dichloro-oxythionaphthene.

Joyce[13] of the Chemical Foundation has produced a mixed thio-indigoid dye by condensing a 2-derivative of 4-methyl-6-chloro-3-oxy-1-thionaphthene with a 3-oxy-1-thionaphthene.

New thio-indigoid dyes have been prepared (Society of Chemical Industry)[14] by reacting on the oxy-thio-naphthene derivatives and the corresponding thio-glycol-*o*-carboxylic acids of anthracene and anthraquinone with five-membered condensed ring

[7] U. S. P. 1,564,218; Dec. 8, 1925.
[8] U. S. P. 1,588,960; June 15, 1926.
[9] U. S. P. 1,586,013; May 25, 1926.
[10] U. S. P. 1,550,075; Aug. 18, 1925.
[11] U. S. P. 1,558,252; Oct. 20, 1925.
[12] U. S. P. 1,590,685; June 29, 1926.
[13] U. S. P. 1,568,458; Jan. 5, 1926.
[14] U. S. P. 1,561,560; Nov. 10, 1925.

systems such as isatins, indoxyls, thioisatins, thioindoxyls or oxythionaphthenes of the benzene, naphthalene, anthracene, and anthraquinone series, acenaphthene-quinones, and the like, their homologs and substitution products, anils and halides.

A new series of dyestuffs has been prepared (Society of Chemical Industry)[15] by condensing 2-halogen anthraquinone 3-carboxylic acid with glycine. By action of condensing agents the indoxyls of 2, 3-anthraquinone series are thus obtained and converted into the indigoid dyestuffs.

The activities of American companies in the field of anthraquinone vat dyes have been confined very largely to improvements in existing methods, whereas a considerable number of vat colors have been prepared in the laboratories of the German dye companies. A process for manufacturing pure anthracene free from carbazol has been described by Weil,[16] which consists in submitting to distillation crude anthracene in the presence of an alkali and in mixture with hydrocarbons boiling between 260° and 315°. From the distillate substantially pure anthracene crystals, with a purity of at least 90%, and from the still residue, carbazol of a high degree of purity can be recovered.

An improved method for the purification of anthraquinone has been worked out by National Aniline & Chemical Co.[17] by vatting anthraquinone with zinc and caustic alkali, filtering from insoluble impurities and oxidizing the filtrate to precipitate anthraquinone, which is finally treated with alkali to remove alkali soluble impurities.

A method has been worked out by the Newport Company[18] for obtaining the ammonium salt of anthraquinone beta sulfonic acid by sulfonating anthraquinone, filtering off the unchanged anthraquinone and making the filtrate slightly alkaline with aqueous ammonia.

A modification of the method for the manufacture of 2-aminoanthraquinone has been made by the National Aniline & Chemical Co.[19] by heating anthraquinone 2-sulfonic acid with aqueous ammonia in the presence of a soluble barium salt and of ammonium chloride.

A process for the preparation of 2,3-diaminoanthraquinone

[15] U. S. P. 1,567,158; Dec. 29, 1925.
[16] U. S. P. 1,548,920; Aug. 11, 1925.
[17] U. S. P. 1,583,297; May 4, 1926.
[18] U. S. P. 1,584,372; May 11, 1926.
[19] U. S. P. 1,564,210; Dec. 8, 1925.

has been described by the Society of Chemical Industry [20] by heating 2-amino-3-bromoanthraquinone with ammonia with or without a copper catalyst.

Benzanthrone derivatives have been made by Cassella [21] by the acid reduction of α-naphthalene azobenzene-*m*-carboxylic acid or its substituents to α-naphthalene hydrazo-benzene-*m*-carboxylic acids which are inverted by acid to 4,4′-diaminonaphthylphenyl-2′-carboxylic acids. The 4,4′-diaminonaphthylphenyl-2′-carboxylic acids [22] are transformed into naphthalenehydrazobenzene-*m*-carboxylic acids by replacing by the Sandmeyer reaction the 2-amino groups of the 4,4′-diaminonaphthylphenyl-2′-carboxylic acids thus obtained by hydrogen, halogen, hydroxyl, methoxyl, etc., and in condensing the products thus obtained into derivatives of benzanthrone, halogenbenzanthrone, hydroxybenzanthrone, etc.

An improvement in the production of N-dihydro-1,2,1′,2′-anthraquinone-azine has been made by the duPont Company [23] by subjecting 2-aminoanthraquinone to the action of fused caustic alkali in the presence of organic hydroxylates, as, for example, sodium butylate.

A process has been described by the Badische Anilin & Soda Fabrik [24] for preparing Indanthrene Blue RS containing both chlorine and bromine. As an example, Indanthrene Blue RS is first chlorinated and then brominated in sulfuric acid.

A process for preparing 2,2′-dibenzanthronyls has been described by the Badische Anilin & Soda Fabrik [25] by condensing benzanthrone or its derivatives with alkaline condensing agents under certain conditions. These intermediate products can be converted into dibenzanthrone dyes by different types of condensing agents.

Recovery of antimony trichloride and nitrobenzene has been effected by the duPont Company [26] from the manufacture of flavanthrone by distilling the filtrate under vacuum and to the distillate adding chlorine to convert all of the antimony present to antimony pentachloride which can then be used again for the conversion of β-aminoanthraquinone to flavanthrone.

As a result of continued study of the condensation of cyanuric

[20] U. S. P. 1,586,911; June 1, 1926.
[21] U. S. P. 1,565,229; Dec. 8, 1925.
[22] U. S. P. 1,588,376; June 8, 1926.
[23] U. S. P. 1,580,700; Apr. 13, 1926.
[24] U. S. P. 1,544,924; July 7, 1925.
[25] U. S. P. 1,564,423; Dec. 8, 1925.
[26] U. S. P. 1,582,328; Apr. 27, 1926.

chloride with amino compounds in the anthraquinone series, the Society of Chemical Industry [27] has found that 5- or 8-amino-2,1-anthraquinone acridones can be condensed with cyanuric chloride to form new vat dyes.

The condensation of benzanthrone with aromatic acid chlorides like benzoyl chloride has been described by the Grasselli Dyestuffs Corp.[28] In the presence of condensing agents, the intermediate product 3-*p*-benzoylbenzanthrone, is formed which then condenses to form 3,4,8,9-dibenzopyrenequinone.

Benzanthrone condensed with benzoic anhydride (Grasselli Dyestuffs Corp.) [29] gives 4,5,8,9-dibenzopyrenequinone.

An improvement in the process of making dibenzanthrone has been described by the National Aniline & Chemical Co.[30] by fusing with caustic potash in the presence of a mineral oil and of a reducing agent like dextrin.

A process for obtaining isodibenzanthrone directly from benzanthrone by treating with an alkali alcoholate has been described by Badische Anilin & Soda Fabrik.[31]

Mixtures of dibenzanthrone and nitrated dibenzanthrone have been found by Badische Anilin & Soda Fabrik [32] to be suitable for producing black shades possessing very good fastness, including fastness to chlorine.

Nitrated dibenzanthrone has been treated by the Badische Anilin & Soda Fabrik [33] with sulfur with or without the addition of suitable carriers, as copper oxide, antimony trisulfide and the like.

Dibenzanthrone has been converted by the Badische Anilin & Soda Fabrik [34] into a chlorinated derivative by the aid of a metallic or metalloid chloride capable of being converted into a chloride of lower valence in the course of the reaction. As an example, dibenzanthrone is heated with antimony pentachloride in trichlorbenzene.

Bright reddish shades of halogen derivatives of dibenzanthrone have been found by Badische Anilin & Soda Fabrik [35] by chlorinating the dibenzanthrone, using chlorosulfonic acid as a medium.

New vat dyes have been obtained by Farbwerke Hoechst [36] by

[27] U. S. P. 1,568,627; Jan. 5, 1925.
[28] U. S. P. 1,564,584; Dec. 8, 1925.
[29] U. S. P. 1,582,475; Apr. 27, 1926.
[30] U. S. P. 1,583,258; May 4, 1926.
[31] U. S. P. 1,580,062; Apr. 6, 1926.
[32] U. S. P. 1,581,638; Apr. 20, 1926.
[33] U. S. P. 1,546,859; July 21, 1925.
[34] U. S. P. 1,562,468; Nov. 24, 1925.
[35] U. S. P. 1,589,303; June 15, 1925.
[36] U. S. P. 1,551,849; Sept. 1, 1925.

heating dihydroxydibenzanthrone with zinc chloride and methylating the product of the reaction with the methyl ester of *p*-toluenesulfonic acid.

An improvement in the process of producing Indanthrene Orange 4R has been found by Newport Company [37] by treating the condensation product of 2,2′-dimethyl-1,1′-dianthraquinonyl in fuming sulfuric acid with bromine in the presence of a catalyst to form dibrompyranthrone.

New vat dyes have been obtained by Badische Anilin & Soda Fabrik [38] by heating naphthanthraquinone with aluminum chloride alone or with aluminum chloride in the presence of phthalic anhydride at elevated temperatures.

Pyrazole-anthrone yellow vat dyes are chlorinated in oleum or chlorosulfonic acid and in the presence of iodine according to the I. G.[39]

Vat dyes suitable for wool have been described by the Grasselli Dyestuffs Corp.[40] and are made by condensing arylamino derivatives of ortho-amino-aryl-mercaptans with arylquinones in which the hydrogen atoms of the quinone nucleus may be substituted by halogen. For example, 3-methyl-5-phenylamino-2,1-aminothiophenol is condensed with chloranil.

Vat dyes for wool are made by the action of thionyl chloride on a diarylidobenzoquinone.[41] Dianilidobenzoquinone, for example, when treated with thionyl chloride produces a very yellow to brownish shade, depending upon the temperature of the reaction.

Considerable work has been carried out on the production of vat dyes from perylene and its derivatives. Zinke and Pongratz [42] have produced halogen derivatives of perylene by the action of hydrochloric acid and hydrogen peroxide on perylene suspended in glacial acetic acid.

Perylene derivatives of quinone character have been obtained by Zinke [43] by treating halogen compounds of perylene with strong sulphuric acid at 130°-140° C.

By the action of aluminum chloride on nitroperylene fast vat dyes have been obtained by Schoepfer.[44]

[37] U. S. P. 1,581,111; Apr. 20, 1926.
[38] U. S. P. 1,582,844; Apr. 27, 1926.
[39] U. S. P. 1,595,549; Aug. 10, 1926.
[40] U. S. P. 1,588,384; June 8, 1926.
[41] U. S. P. 1,544,441; June 30, 1925.
[42] U. S. P. 1,580,708; Apr. 13, 1926.
[43] U. S. P. 1,590,661; June 29, 1926.
[44] U. S. P. 1,574,116; Feb. 23, 1926.

Perylene quinone has been chlorinated by Zinke and Schoepfer [45] and has been boiled with aniline to produce vat dyes of greenish yellow shades on cotton.

By the reduction of the corresponding nitro derivatives, Zinke [46] has obtained amino perylene quinones.

The dibenzoate of dihydroxyperylene when heated with aluminum chloride has been found by Zinke and Hanselmayer [47] to produce a new vat blue dye.

Eckert and Greune [48] have made fast vat dyes by condensing the dianhydride of 1,4,5,8-naphthalenetetracarboxylic acid with an *o*-diamine. *o*-Phenylenediamine, for example, produces bright yellowish red, or with 4-chloro-1,2-diaminobenzene, a bright reddish brown.

The field of anthraquinone chemistry offers attractive possibilities of further exploitation by the research staffs of our universities. A large amount of work has already been carried out, particularly on the manufacture of dyestuffs, by laboratories of the companies offering vat colors. A considerable portion of this work, however, has never been published, but only the processes and products appearing to have some commercial importance have appeared in the patent literature. It has been a field which has not attracted in the past our university laboratories, although one of the most important fields of dyestuff chemistry on account of the remarkable fastness of these dyes to washing, light and chlorine. As a class, they are unsurpassed in these properties by any other group of dyestuffs and shall continue to become even more important than they have been in the past because of the insistent demand of the American public for fast colors. The industry would welcome the interest of our universities in this field of research and is ready not only to supply the intermediates that are commercially available, but to extend the service of its laboratories to study the application of products to the fiber.

[45] U. S. P. 1,569,111; Jan. 12, 1926.
[46] U. S. P. 1,586,729; June 1, 1926.
[47] U. S. P. 1,586,730; June 1, 1926.
[48] U. S. P. 1,588,451; June 15, 1926.

Chapter XX.

Pharmaceutical Chemistry.

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Pharmaceutical chemistry, if the term be used in its broadest sense, possesses so wide a scope that a review of progress would involve consideration of the chemical aspects of therapeutic agents from botanical sources, inorganic compounds, substances of animal origin, products of organic synthesis and materials of bacterial derivation or those produced by other biologic methods, besides those complex mixtures representing varied ways of presenting the combined medicinal effects of many of these. Such breadth of treatment in this chapter is, however, unnecessary as other chapters deal with biologic medicinals and those obtained by organic synthesis. Nevertheless, because of the ramifications of pharmaceutical chemistry there may be some unintentional overlapping, and greater chance that work of value may be overlooked.

Probably no two reviewers would select the same material as of proper significance for inclusion here. This chapter cannot be a full report of all progress in pharmaceutical chemistry nor a compendium of information on the year's work but the writer only hopes it may point very briefly to some useful advance steps that have been taken and perhaps through this suggest where others may be attempted.

During the twelve months covered by this review there has been evidence of renewed interest in the possible medicinal properties of plants and their constituents. These have doubtless been stimulated to some extent by the voluminous work of J. J. Chen and others on the alkaloids of the Chinese drug, Ma Huang (Ephedra vulgaris). Known for forty years and even previously synthesized, they languished in obscurity until a new medicinal effect was discovered in the preceding year. This action was

the power possessed by the alkaloid ephedrine to cause rise in blood pressure when given either hypodermically or by mouth. The best summary of this work is in a paper by Chen and Kao,[1] containing a very complete bibliography, published since the end of the period covered by this review.

Clark and Offord[2] report investigations of locality, altitude, time of collection and other factors on stramonium and conium of British Columbia, and a study of micro-chemical reactions of the location of the oil in different parts of chenopodium of Philippine origin is described by J. K. Santos.[3]

A mixture of alkaloids has been obtained from Ceanothus americanus and from this at least one definite, crystalline alkaloid has been isolated and studied by A. H. Clark.[4] The alkaloids are reported to have the unique physiological effect of increasing the coagulability of the blood when administered orally.

It should be remarked in this connection that quite a number of investigations of both new and old medicinal plants have been carried out in various other countries.

Those drugs of cathartic action depending for their activity upon anthraquinone derivatives continue to be a fertile field for investigation, partly because of their importance as therapeutic agents and our need of better chemical knowledge concerning them, and partly because the difficulties in the way of obtaining exact and dependable data make any important progress something to be considered a real achievement. Because of this relation to American researches, the two following are first mentioned.

Bridel and Charaux[5] describe a new glucoside from Rhamnus catharticus which they call rhamnicoside.

The tetrachlor-derivatives of various aloins are described by Leger[6] and their production considered as a means of evaluating aloes of different origin.

Beal and Katti,[7] continuing investigations previously carried out by Beal and other assistants, contribute the most voluminous and painstaking work of the year on cathartic drugs in an endeavor to perfect a quantitative determination of anthraquinone bodies in this class of drugs, especially in cascara. A large

[1] J. Am. Pharm. Assoc., **15**: 625; 1926.
[2] Trans. Roy. Soc. Can. (3), **20** III: 153; 1926.
[3] Philippine J. Sci., **28**: 529; 1925.
[4] Am. J. Pharm., **98**: 147; 1926.
[5] Compt. rend., **180**: 1047, 1219; 1925. *Cf.* Ann. chim. (10), **4**: 79; 1925.
[6] J. pharm. chim. (8), **3**: 305; 1926.
[7] J. Am. Pharm. Assoc., **14**: 865; 1925.

amount of interesting and valuable data is given, though the authors do not consider themselves justified as yet in drawing any positive conclusions from their work. There is very much yet to be done on this problem, especially in finding a chemical method of assay that will be a definite measure of physiological effect.

A study of certain colorimetric reactions of aloes, cascara, frangula and rhubarb, and the significance of the same is made by Berardi and Canan.[8]

It is interesting to note that U. S. Patent 1,586,039 covers a laxative mixture of $MgCO_3$ with 1,8-hydroxyanthraquinone and 1,586,040 is similar but using MgO.

In spite of innumerable publications dealing with the chemistry and pharmacology of digitalis no year seems complete without its added record of such investigation. Few vegetable drugs are more deserving of intensive study or present greater difficulties in the way of obtaining exact and dependable data. During the past year Schneider [9] discusses experiments with a new method of assay as does also Berardi,[10] while Tainter [11] gives a summary of long investigation of the relation between p_H value and stability of digitalis infusions.

Aside from the investigation of ephedrine already mentioned, there has been comparatively little work in this country on alkaloids during the past year. A paper by Schulz [12] on berberine while being almost wholly a review is especially interesting because of the very full bibliography accompanying it. Quite a number of studies of new alkaloids and much work on the synthesis of old and well known substances and their derivatives are to be found in records of research from various foreign countries.

Beath [13] describes new work on the alkaloids and activity of Aconitum columbianum.

The quantitative determination of alkaloids by potentiometric methods has been further developed by Wagener and McGill [14] using a quinhydrone electrode, by Popoff and McHenry [15] using a platinum electrode, and by Krantz,[16] and it might not be amiss

[8] J. Am. Pharm. Assoc., **15**: 189; 1926.
[9] J. Am. Pharm. Assoc., **14**: 128; 1925.
[10] J. Am. Pharm. Assoc., **15**: 563; 1926.
[11] J. Am. Pharm. Assoc., **15**: 255; 1926.
[12] J. Am. Pharm. Assoc., **15**: 33; 1926.
[13] J. Am. Pharm. Assoc., **15**: 265; 1926.
[14] J. Am. Pharm. Assoc., **14**: 288; 1925.
[15] J. Am. Pharm. Assoc., **14**: 473; 1925.
[16] J. Am. Pharm Assoc., **14**: 294; 1925.

to mention also the work of Muller [17] using the hydrogen electrode. The suitability of different indicators in alkaloidal titration is reported on by H. Wales.[18]

An unusual and interesting method of identifying alkaloids of ipecac is described by Palkin and Wales [19] who prepare certain azo dyes from the alkaloids and obtain characteristic absorption spectra from solutions.

While not truly a chemical research the investigation by Myers and Thiems [20] of the fungicidal properties of various volatile oils is of sufficient interest to warrant recording here.

Among the fixed oils of interest from a medicinal standpoint there are two that in the past year have received the major share of attention, namely chaulmoogra and cod liver oils.

Concerning the former much synthetic work is referred to in the chapter on "Organic Medicinals"; and as in some ways related to this there may be mentioned the work of Nord and Schweitzer [21] who believe they have shown some relation between optical activity and physiological action. With regard to cod liver oil practically all research work classifies under nutritional and biological chemistry though Dubin [22] describes a method for producing an antirachitic concentrate.

In the field of metallic compounds Masucci and Slothower [23] conclude that iron cacodylate so prepared as to be colloidal in character is much less toxic for intravenous use than if the iron is in the ionic state. Numerous organic preparations of arsenic, bismuth and mercury properly belong under the heading of organic medicinals or organic chemistry but several recently issued patents may be noted here—U. S. Patent 1,558,584 on complex gold compounds, 1,561,535 on organic antimony compounds, and 1,589,599 on certain soluble organic compounds of mercury, arsenic, antimony and bismuth.

One foreign investigation most likely to stimulate further research on the medicinal effects of minute amounts of some metals is that of Bertrand and Machebouef [24] on the influence of extremely small quantities of nickel and cobalt on the action of

[17] Z. Elektrochem., **30**: 587; 1924.
[18] Ind. Eng. Chem., **18**: 390; 1926.
[19] J. Am. Chem. Soc., **47**: 2005; 1925.
[20] J. Am. Med. Assoc., **84**: 1895; 1925.
[21] Biochem. Z., **156**: 269; 1925.
[22] J. Am. Pharm. Assoc., **14**: 215; 1925.
[23] Am. J. Pharm., **97**: 587; 1925.
[24] Compt. rend., **182**: 1504; 1926.

insulin and the possibility that such substances alone may produce effects resembling those of insulin.

In the realm of chemistry of gland products the outstanding research is that reported by Abel [25] on the production of crystalline insulin. He describes a crystalline substance containing labile sulfur, giving biuret, Millon, Pauly and ninhydrin reactions, which is very active in producing hypoglycemia.

Among studies during the year of the active hormone of the parathyroid glands may be mentioned especially those of Hjort, Robison and Tendick [26] on methods of producing active extracts and data on their stability, also Collip [27] describing method of production and standardization of an active extract.

An addition to available chemical data on the Corpus luteum is made by Hart and Heyl,[28] while Fullerton and Heyl [29] report studies of Liquor Folliculi and the same authors [30] give data from an investigation of the proteins of ovarian residue, to which study they add further data.[31]

An example of a previously known chemical substance for which a new medicinal use has been discovered is found in tetrachlorethylene as an anthelmintic (Hall and Shillinger [32] and Schlingman [33]). A similar case is that of *o*-iodoxybenzoic acid as used for the treatment of arthritis reported by Young and Youmans.[34]

Among general anæsthetics Riggs [35] compares the anæsthetic properties of ethylene, propylene, butylene and smylene, while several minor chemical investigations of ether are noted as are also two Dutch patents 13,636 and 13,637 for producing ether of exceptional purity by first preparing benzidine crystals containing ½ mol. ether of crystallization and from these distilling the ether in an atmosphere of hydrogen.

New chemical substances that have recently come into use for cholecystography are tetraiodophenolphthalein and phenoltetraiodophthalein as well as the corresponding tetrabromo compounds.

A committee of the American Drug Manufacturers' Associa-

[25] Proc. Nat. Acad. Sci., 12: 132; 1926. *Cf.* Abel, Geiling, Alles and Raymond, J. Pharmacol., 25: 423; 1925.
[26] J. Biol. Chem., 65: 117; 1925.
[27] Proc. Nat. Acad. Sci., 11: 484; 1925.
[28] J. Am. Pharm. Assoc., 14: 770; 1925.
[29] J. Am. Pharm. Assoc., 15: 16; 1926.
[30] J. Am. Pharm. Assoc., 15: 18; 1926.
[31] J. Am. Pharm. Assoc., 15: 549; 1926.
[32] Am. J. Trop. Med., 5: 229; 1925.
[33] J. Am. Vet. Med. Assoc., 68: 225, 741; 1925.
[34] J. Pharmacol., 27: 252; 1926.
[35] J. Am. Pharm. Assoc., 14: 380; 1925.

tion has been investigating the effect of p_H on the activity of certain local anesthetic solutions and the change in p_H with age, but final conclusions have not yet been reached.

In the field of analysis and standardization of drugs numerous reports to be found in the J. Assoc. Official Agr. Chem., 8: 499, 572; 1925, are of interest and value.

Besides other patents already mentioned the following are of interest:

Brit. Pat. 230,432—Ureides of hexahydrobenzoic acid and derivatives, having sedative and narcotic properties.

Brit. Pat. 230,329, 230,404 and 231,120—Combinations of dyes and yeast as antiseptic compounds.

Brit. Pat. 230,089—Picrates of various local anæsthetics for use as antiseptics and anæsthetics.

As an index to pharmaceutical investigations the monthly "Bibliography of Pharmaceutical Research" by DuMez in the *J. Am. Pharm. Assoc.* may be consulted.

A summary of the very numerous researches in different phases of pharmaceutical chemistry and a statement of the location of such work which would take considerable space, is scarcely necessary here in view of the excellent census of Pharmaceutical Research prepared under the auspices of the National Conference of Pharmaceutical Research and available in printed pamphlet form from the chairman of this conference, Dr. H. V. Arny, N. Y. College of Pharmacy.

Suggestions for Future Research.

The Committee of Revision of the U. S. P. has just prepared for distribution a list of subjects connected with the Pharmacopœia for further investigation, and this list will be quite widely published in pharmaceutical and medical journals. Copies of it can also be obtained from Mr. E. Fullerton Cook, 636 South Franklin Square, Philadelphia, who is Chairman of the Revision Committee.

Many avenues of research in pharmaceutical chemistry are quite obvious and a little study reveals many more, but a brief list of very broad subjects will not be amiss.

1. The endocrine glands, their active principles and methods of determining activity.
2. The digestive enzymes such as pepsin, pancreatin, etc., their exact nature and more accurate methods of standardizing.

3. Antiseptics that may be used intravenously,—destructive to pathogenic bacteria and relatively harmless to human beings.
4. Anæsthetics.
5. Hypnotics.
6. Cathartics,—exact chemical nature and methods of standardization.
7. Possible new physiological effects of chemicals previously known.
8. Investigation of plant constituents, especially of new drugs.
9. Effect of p_H on stability of liquid preparations of potent drugs.
10. The exact nature of toxic products of bacterial growth.
11. Use of spectrophotometer in the study of solutions.

Chapter XXI.

Organic Medicinals.*

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It is encouraging to note that here in the United States cooperation between organic chemistry and medicine is steadily growing more frequent and more intimate, as the organic chemists perceive their splendid opportunities for service in this field and the medical men recognize the character and extent of the assistance thus available. Replies received to a questionnaire sent out to 793 of our organic chemists and pharmacologists show that over 300 of these scientists are either already engaged in coöperative research of the kind mentioned or will gladly participate in such work.

The problem of the connection between chemical constitution and physiological effect is an exceedingly complicated, difficult and baffling one, but progress is being made towards its solution and slowly but surely we are advancing towards that goal.

Within the brief limits of this review only a few of the many interesting researches of the past year can be considered, and they are selected from those fields in which the Committee on Chemical Research on Medicinal Substances of the National Research Council has been in contact with the workers.

In addition to the researches noted under the special headings later, recently published articles of general interest are those of Arny [1] on the evolution of synthetic medicinal substances, of Adams [2] on synthetic versus natural products, and of Leech [3] on the standardization and evaluation of medicinals.

* Comprising in part the report of the Committee on Chemical Research on Medicinal Substances for the year 1925-1926. Marston T. Bogert, Chairman, Roger Adams, H. V. Arny, George D. Beal, Arthur W. Dox, Frederick W. Heyl, Arthur J. Hill, Treat B. Johnson, Charles H. LaWall, W. Lee Lewis, R. R. Renshaw, and Frank C. Whitmore.

[1] Ind. Eng. Chem., **18**: 949; 1926.
[2] Ind. Eng. Chem., **18**: 1182; 1926.
[3] Ind. Eng. Chem., **18**: 953; 1926.

Special Fellowships and Scholarships. It is worth noting that special fellowships and scholarships for investigation of organic medicinals have been established in the following institutions:

University of Chicago.—The Seymour Coman Research Fellowship, of $2000 to $3000 per annum, in chemistry applied to medicine.

Columbia University.—The Ferguson Fellowship, of $1000 per annum, awarded every other year, for investigation and research in synthetic drugs and medicinals. Also a Research Assistantship, of $1800 per annum, for the synthesis and investigation of organic compounds of possible therapeutic value.

Northwestern University.—About 12 fellowships for graduate students, with stipends up to $1000-$1200 per annum, have been available for researches in the organic chemistry of arsenic and of mercury.

Additional Funds. It is unquestionably and pathetically true that thousands of human lives and an immense amount of suffering depend upon the speed with which we can reach some of the goals toward which our workers are now striving. The chief handicap today in the prosecution of their work is lack of adequate financial assistance, and it is to be hoped that our public-spirited citizens will come to the aid of these altruistic undertakings which mean so much for the progress of civilization and for human happiness.

Researches in Selected Fields.

Acridine Medicinals. New diamino acridines, both of proflavine and of neutral acriflavine type, carrying the amine groups in positions 3:7, instead of 2:8, have been synthesized by Bogert and Lauffer [4] at Columbia University and are now being tested pharmacologically by Hirschfelder at the University of Minnesota. Their therapeutic properties seem to be much the same as their prototypes, and it is too early to say yet whether they are in any respects preferable to the older preparations.

Anthraquinone Drugs. At the University of Illinois, Beal and his co-workers [5] have been studying the nature of the combined anthraquinones in various well known drugs, for the purpose of developing a satisfactory quantitative method for their

[4] Lauffer, Dissertation, Columbia Univ., 1926.
[5] J. Am. Pharm. Assoc., 14: 865; 1925.

estimation and an accurate colorimetric process involving the use of the spectrophotometer. These investigations have been aided by a grant from Parke, Davis & Company. The discovery by Adams and Jacobson [6] of the organic laboratories of the same university, of a method of synthesizing anthraquinone derivatives from opianic acid, promises very valuable results in this group, since it opens the way for the preparation of compounds carrying the substituent groups in known positions.

Arsenicals. A very useful and suggestive contribution is Christiansen's "Future Research in the Field of Organic Arsenicals." [7]

At Northwestern University, Lewis, Whitmore and Palmer, with the aid of grants from the Public Health Institute of Chicago, are developing new lines of organic arsenicals, including also those of aliphatic type. The physiological effects of these new compounds are being studied by Loevenhart at the University of Wisconsin and the more promising ones are being tested clinically by W. F. Lorenz at the Mendota Hospital for the Insane, with special reference to their value in the treatment of neurosyphilis.[8] Loevenhart, Lorenz and their associates have described carefully standardized methods of determining the therapeutic value of new arsenicals and have published an important communication [9] on the chemotherapy of neurosyphilis and trypanosomiasis. Lewis and Bent [10] have described the preparation and properties of 3,4-diaminophenylarsonic acid and some of its derivatives.

Raiziss, at the University of Pennsylvania, in coöperation with Severac and Moetsch,[11] has been carrying out a careful study of the chemotherapy of sulfarsphenamine, comparing it with arsphenamine and with neoarsphenamine; and with Brown [12] on the effect of organic compounds of arsenic, mercury and bismuth on the kidneys of animals judged by the non-protein nitrogen and urea content of the blood, as a result of which he finds that mercury compounds have the highest toxicity, arsenic compounds the lowest, and that among the latter neoarsphenamine is the least toxic. From the Hygienic Laboratory of the U. S. Public Health

[6] J. Am. Chem. Soc., **46**: 2788; 1924. **47**: 283, 2011; 1925.
[7] Ind. Eng. Chem., 17: 1270; 1925.
[8] Lorenz, Loevenhart, Reitz and Eek, Am. J. Med. Sci., **168**: 157; 1924.
[9] Loevenhart and Stratman-Thomas, J. Pharmacol., **27**: 234; 1926.
[10] J. Am. Chem. Soc., **48**: 949; 1926.
[11] J. Am. Med. Assoc., **83**: 1734; 1924.
[12] Arch. Permitol. Syphilol., 10: 1; 1924. Ber. ges. Physiol. exptl. Pharmacol., **30**: 810; 1924.

Service, Voegtlin [13] contributes important articles on the pharmacology of arsphenamine and related arsenicals; and, with Dyer and Leonard [14] on the specificity of the arsenic receptor in the higher animals.

Chaulmoogric Acid and Related Compounds. Because of the significance of these compounds in the treatment of leprosy, the work now going on at the University of Illinois under the direction of Adams is of unusual importance. Based upon the brilliant antecedent work of Power and his associates,[15] Shriner and Adams [16] have established the formula of chaulmoogric acid as I and of hydnocarpic acid as II.

$$\begin{matrix} CH=CH \\ | \qquad\quad \\ CH_2—CH_2 \end{matrix} > CH(CH_2)_{12}COOH$$

(I)

$$\begin{matrix} CH=CH \\ | \qquad\quad \\ CH_2—CH_2 \end{matrix} > CH(CH_2)_{10}COOH$$

(II)

A racemic homolog of chaulmoogric and hydnocarpic acids, with a short side chain has been synthesized, as well as the homochaulmoogric and homohydnocarpic acids.[17] Bacteriological tests on these and on other closely related compounds are expected to throw some light upon the influence of the length of the side chain in determining therapeutic properties, as well as upon the relative value of an odd or even number of carbon atoms in the molecule. The synthesis has been completed of cyclohexane derivatives containing an omega carboxylated side chain varying in length from 1 to 13 carbon atoms, and work is progressing upon the analogous cyclopentane derivatives.

Cinchophen Types. In the organic laboratories of Columbia University, new cinchophen types have been synthesized and among those previously prepared [18] one containing the quinazoline nucleus is being tested pharmacologically by Rockwood of the State University of Iowa and looks promising, in that it is rela-

[13] Physiol. Rev., **5**: 63; 1925.
[14] J. Pharmacol., **25**: 297; 1925.
[15] Power and Gornal, J. Chem. Soc., **85**: 838, 851; 1904. Barrowcliff and Power, J. Chem. Soc., **91**: 557; 1907.
[16] J. Am. Chem. Soc., **47**: 2727; 1925.
[17] Noller and Adams, J. Am. Chem. Soc., **48**: 1080; 1926.
[18] J. Am. Chem. Soc., **46**: 1700, 1702; 1924.

tively non-toxic and appears to have definite value in reducing the uric acid content of the blood. The research is being aided by a grant from the Sigma Xi Research Fund.

Adams and his collaborators, at the University of Illinois, have turned their attention to the preparation of arsenic derivatives of cinchophen and have prepared and studied arsonophenylcinchoninic acid and various derivatives thereof, all of which proved to be more toxic and less trypanocidal than arsphenamine or arsanilic acid.[19]

Hypnotics. Shonle, of Eli Lilly & Company, is engaged in the compilation of a bibliography of hypnotics from the chemical and clinical standpoints. Dox,[20] of Parke, Davis & Company, recently prepared and examined ethylphenethylbarbituric acid and related derivatives and reported that certain of these compounds exhibited a very powerful hypnotic effect. He [21] has also investigated the pharmacological action of the tetraalkylsuccinimides and found them toxic, causing muscular incoördination and convulsions without any evidence of sedative action. Cretcher and co-workers [22] at the Mellon Institute have been engaged upon the preparation and study of the hypnotic effects of certain hydroxylated alkyl barbituric acids. Hill [23] of Yale University has prepared a number of new barbituric acid derivatives and made some interesting observations on the connection between pharmacological action and chemical constitution in this series. Judged by their effects upon white rats, Volwiler [24] finds that as hypnotics the alkylallylbarbituric acids decrease in desirability in the following order: butyl, isobutyl, diallyl, propyl, isopropyl or secondary butyl, isoamyl, ethyl.

Internal Antiseptics. Under the trade name of "Caprokol," *n*-hexyl resorcinol (2,4-dihydroxy-*n*-hexylbenzene) is being marketed and appears to be proving a most valuable urinary antiseptic, with a phenol coefficient of approximately 45. This coefficient falls precipitately when the *n*-hexyl group is replaced by lower or by higher alkyls. The compound has been admitted by the American Medical Association to the 1926 edition of its New and Nonofficial Remedies. Its discovery was made pos-

[19] Ogden and Adams, J. Am. Chem. Soc., **47**: 826; 1925. Calvery, Noller and Adams, J. Am. Chem. Soc., **47**: 3058; 1925.
[20] J. Am. Chem. Soc., **46**: 2843; 1924.
[21] J. Am. Chem. Soc., **47**: 1471; 1925.
[22] Cretcher, Koch and Pittenger, J. Am. Chem. Soc., **47**: 3083; 1925.
[23] Hill and Keach, J. Am. Chem. Soc., **48**: 257; 1926.
[24] J. Am. Chem. Soc., **47**: 2236; 1925.

sible through the earlier work of Treat B. Johnson of Yale and it has been introduced through the investigations carried out in the laboratories of Sharp and Dohme [25] of Baltimore, in association with Veader Leonard [26] of Johns Hopkins University and others.[27]

Lead. The poison hazards of tetraethyl lead have been the subject of extensive investigation by Midgley,[28] Salls,[29] Shrader,[30] Hamilton, Reznikoff and Burnham,[31] Kehoe,[32] Norris and Gettler,[33] and others, because of the utilization of this compound in the production of the so-called antiknock "Ethyl Gas."

Local Anesthetics. Investigations on derivatives of *p*-hydroxymethylbenzoic acid and upon amidines of holocaine type have appeared from the laboratory of Hill [34] of Yale University, where an extensive monograph and bibliography of local anesthetics is now nearing completion. Adams,[35] of the University of Illinois, in collaboration with a number of his students, has published a valuable paper on the chemical constitution, physiological action and physical properties of a series of alkyl *p*-aminobenzoates, using goldfish for the physiological tests. Johnson, of Yale University, in collaboration with Roberts,[36] has prepared certain derivatives of diphenic acid which have been found to possess the properties of local anesthetics. At the University of Minnesota, Jensen and Hirschfelder [37] have examined the local anesthetic and antispasmodic actions of some ethers and esters of saligenin and found them too pungent and irritating for clinical administration either orally or subcutaneously.

Mercurials. Whitmore at Northwestern University has been continuing his work on the preparation of new types of organic mercurials and in studying their chemical and physiological properties, while their pharmacological examination is being conducted by Loevenhart at the University of Wisconsin.

[25] Dohme, Cox and Miller, J. Am. Chem. Soc., **48**: 1688; 1926. Dohme, Brit. Pat. 219,922; July 31, 1923. Brit. Pat. 223,190; Oct. 9, 1923. Brit. Pat. 224,913; July 31, 1922.
[26] Leonard, Science, **62**: 408; 1925. Leonard and Wood, J. Am. Med. Assoc., **85**: 1855; 1925. Leonard and Frobisher, J. Urol., **15**: 1; 1926.
[27] Henline, J. Urol., **14**: 119; 1925. Brown, J. Am. Med. Assoc., **86**: 668; 1926.
[28] Ind. Eng. Chem., **17**: 827; 1925.
[29] Nation's Health, **7**: 169; 1925.
[30] Am. J. Pub. Health, **15**: 213; 1925.
[31] J. Am. Med. Assoc., **84**: 1481; 1925.
[32] J. Am. Med. Assoc., **85**: 108; 1925.
[33] J. Am. Med. Assoc., **85**: 818; 1925.
[34] Hill and Rabinowitz, J. Am. Chem. Soc., **48**: 732; 1926.
[35] Adams, Rideal, Burnett, Jenkins and Dreger, J. Am. Chem. Soc., **48**: 1758; 1926.
[36] J. Am. Chem. Soc., **47**: 1396; 1925.
[37] J. Pharmacol., **24**: 423; 1925.

Onium Compounds. Reid Hunt at Harvard and Renshaw [38] at New York University have continued their investigations in this field, and have published papers covering the synthesis of new products and their pharmacology, as well as on the mobilities of certain onium ions.[39] Arsonium, stibonium, phosphonium and sulfonium compounds were included in the research.[40] With the aid of some of these new products, Hunt has been able to get a more specialized control over the peripheral nervous system than has been possible heretofore.

Sulfur and Selenium Medicinals. Many new thiazole and selenazole derivatives have been synthesized in the organic laboratories of Columbia University and are now undergoing pharmacological investigation.[41] Perhaps the most interesting are the arsenical derivatives, some of which show considerable promise.

Tuberculosis. Johnson and his associates [42] at Yale University are continuing their study of the chemical composition of tubercle bacilli; and the results of this study will be followed with very deep interest. They [43] have recently made the noteworthy discovery that 5-methylcytosine is present in tuberculinic acid, the nucleic acid of the tubercle bacillus.

Universities Participating in the Work.

For the benefit of prospective graduate students and others planning to pursue investigations in the application of organic chemistry to the preparation and examination of new compounds of possible therapeutic value, information is supplied below as to the main lines of such research now under way in some of our leading educational institutions. It should be clearly understood that this list records only chemical investigations and does not cover the pharmacological side.

Columbia University. Thiazoles, selenazoles, cinchophens, acridines, quinazolines, triphenylmethane dyes, phenacetines, phenolic antiseptics, glycogen.

Iowa State College. Organic magnesium compounds.

Johns Hopkins University. Sulfur and selenium derivatives, and antimonials.

[38] Renshaw, Science, **62**: 384; 1925. Renshaw, Bacon and Roblyer, J. Am. Chem. Soc., **48**: 517; 1926. Renshaw and Bacon, J. Am. Chem. Soc., **48**: 1726; 1926.
[39] Bencowitz and Renshaw, J. Am. Chem. Soc., **47**: 1602; 1925. **48**: 2146; 1926.
[40] J. Pharmacol., **25**: 315; 1925.
[41] J. Am. Chem. Soc., **47**: 3078; 1925. 48: 223, 248, 783; 1926. Proc. Nat. Acad. Sci., **11**: 768; 1925.
[42] Johnson and Coghill, J. Biol. Chem., **63**: 225; 1925.
[43] Johnson and Coghill, J. Am. Chem. Soc., **47**: 2838; 1925.

New York University. Onium compounds.

Northwestern University. Arsenicals, mercurials and organic bismuth compounds.

University of Illinois. Chaulmoogric and hydnocarpic acids and related compounds, local anesthetics, anthraquinones and organic bismuth compounds.

University of Maryland. Organic gold compounds and arsenicals.

University of Pennsylvania. Arsenicals.

University of Wisconsin. Local anesthetics.

Yale University. Antiseptics, chemistry of tubercle bacillus, pyrimidines, nucleotides, thioamides and local anesthetics.

Research Suggestions.

Among the innumerable opportunities for research in the utilization of organic chemistry in the service of medicine, a few only can be emphasized here.

1. Remedies for cancer, pernicious anemia, phthisis, epidemic encephalitis, acute anterior poliomyelitis, chronic arthritis and epilepsy.
2. Isolation, identification and synthesis of the active principles of endocrine secretions, of hormones and of antibodies, involving also the possibility of the synthesis of products which while not identical with these active principles may be closely related to them chemically and of equal or greater therapeutic value.
3. Synthesis of an intestinal antiseptic of high therapeutic index.
4. The synthesis of a satisfactory cathartic, as a substitute for cascara; of a suitable substitute for digitalis, and of new styptics.
5. The chemistry of bacteria and other microörganisms.
6. The part played by normal constituents of the host in the physiological action of drugs.
7. The connection between constitution and physiological action in groups of closely related and carefully purified organic compounds, like the triphenylmethane dyes, for example.
8. Pharmacological studies of series of organic compounds not hitherto examined as to their physiological properties.
9. The study of drugs influencing peristalsis, the renal function, the heart or the respiration.
10. The synthesis of organic lead compounds which shall combine the curative properties claimed for metallic lead, in the treatment of cancer, with the deep penetration characteristic of tetraethyl lead.
11. The function of enzymes in disease.
12. The chemical investigation of secretagogues, like gastrin and secretin.
13. The preparation of new pharmaceuticals from petroleum.
14. Carefully standardized methods of pharmacological testing.

Chapter XXII.

Proteins.

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In order to make the analysis of the work done in America in the field of protein chemistry comprehensible to those who have not followed very closely the recent progress in this chapter of chemistry, it seems desirable to preface the critical review by a very brief sketch of the problems which today engage the attention of protein chemists.

The methods employed for the study of the structure and the conduct of the protein molecule are those of organic chemistry and physical chemistry and those of biology. It may be advantageous to summarize separately the work accomplished by each method.

Structural Chemistry of Proteins. The systematic study of the structure of the protein molecule is of comparatively recent date and there is little wonder that an agreement of views has not been reached. The older, which one may term classical, and the newer conceptions of the structure of the molecule differ radically from one another. The points of difference in general terms are the following: According to the older view the component units of the protein molecule, the amino acids, are linked among themselves through primary valence forces, and the elementary units of the protein molecule are those amino acids which are obtained on hydrolysis of proteins.

Of the newer theories the more radical deny both of these cardinal principles. They assume that the unit elements of the protein molecule are not amino acids, but cyclic compounds, which according to some authors are composed of ordinary amino acids and which according to others are composed of amino acids having a different structure from those obtained on hydroly-

sis, but into which they are transformed in the process of hydrolysis. Furthermore, they assume that the unit elements are held together in the protein molecule by forces other than those of primary valence.

The more moderate critics of the older views admit the existence in the protein molecule of comparatively long peptide chains but along with these they suggest the presence also of complex cyclic compounds. In fact, such a possibility had already been pointed out by E. Fischer.

In detail the new theories of the structure of the protein molecule are the following:

1. The protein molecule is composed of peptide chains of different dimensions which are linked together in ureid-linkings through $O=C$ groups or through polyhydric alcohols (Brigl).

2. It consists of ketopiperazine rings held together by secondary valences (Ssadikov, Zelinski, Abderhalden, M. Bergmann).

3. It is composed in the main of complex pyrrole derivatives. This theory assumes that the amino acids obtained on hydrolysis are not pre-formed in the protein molecule (N. Troensegaard).

The number and the variety of theories are sufficient proof that conclusive evidence has not yet been offered in favor of any one. Many of the new conceptions of the molecular structure of the protein molecule are quite ingenious. The observations of Bergmann on polymerization of unsaturated ketopiperazines are particularly important and interesting, but by themselves do not justify the conclusion that proteins are built in an analogous manner.

In recent years Abderhalden has been particularly active in searching for experimental evidence in support of the ketopiperazine structure of proteins. First, he isolated several ketopiperazines from the cleavage products of proteins. He then found that the product of hydrolysis of the proteins on reduction yielded piperazines which are reduction products of the ketopiperazines. He further found that the products of oxidation of ketopiperazines were different from those of peptides and that among the oxidation products of proteins identical substances to those obtained on oxidation of ketopiperazines were found.

However, the evidence of Abderhalden has been challenged on the basis of the observations that peptides are very easily

transformed into ketopiperazines under the conditions of ordinary protein hydrolysis (Brigl, Dakin, Levene and Simms, and others). Also recent work on enzymatic hydrolysis of proteins has led Waldschmidt-Leitz to decide against the cyclic theory of protein structure.

Thus, the opponents of the older theory of protein structure point out that amino acids may be the secondary products and that the cyclic units are the primary components while the opponents of the new theories reverse the view as to which is the primary and which the secondary product.

There are problems, however, which are of equal importance to advocates of the older as well as to those of the newer theoretical conceptions. These are, first, the quantitative isolation of the components of the individual proteins. Much advance in this direction was made in recent years by Dakin. Second is the purification of the individual proteins.

Physical chemistry contributed more to the understanding of the colloidal behavior of proteins than to the details of molecular structure. Associated with these problems are those on enolization and on formation by the protein molecule of not readily ionizable complex salts. Excellent summaries of the physical chemistry of proteins were published recently in the Physiological Reviews, one by David I. Hitchcock and the other by Edwin Cohn.

With this background of the general status of protein chemistry of today it will be easier to estimate the true value of the American contribution of the past year. It must be said at the outset that the interest of American chemists in this field of research was not as great as that of their European colleagues.

Methods of Organic Chemistry.

There are two aspects of earlier work in protein chemistry which may be regarded as peculiarly American. One is the isolation of pure vegetable proteins. In this field the classical contributions of T. B. Osborne remain the inspiration of the younger workers.

In the past year, contributions in this direction were made by Jones, Gersdorff and Moeller,[1] who isolated from the bark of the locust tree albumins, globulins and proteases. The interesting point of this work—a point, however, which needs further investigation—is the finding that some of the proteins seemed to

[1] J. Biol. Chem., 64: 655; 1925.

possess enzymatic properties (urease and amygdalase). Further, D. B. Jones and T. A. Csonka [2] have analyzed the proteins of the cottonseed and among these discovered a protein which contains 16.5% of pentose and only 0.194% of phosphorus, and, hence, most likely is not a nucleoproteid. The mode of union of the pentose to the protein molecule should be investigated.

In connection with the preparation of proteins the work of E. M. Shelton and T. B. Johnson [3] should also be mentioned, in which a method was given for the preparation of sericin from various samples of silk.

The second field of research in protein chemistry is one in which American work attained much prominence through the contributions of D. D. Van Slyke, Dakin and Folin. It is the field of analytical methods. In the past year a method for estimation of tyrosine was developed by M. T. Hanke [4] and a method of sulfur estimation in proteins by means of feeding experiments was given by H. C. Sherman and Ella Woods.[5]

The search for new components was also continued in the course of the past year and R. A. Gortner and W. Hoffman [6] described a substance which from the elementary analysis of the phenylisocyanate derivative they concluded to be hydroxyaminobutyric acid. The substance, however, was not isolated in a free state and further evidence of the nature of the substance is still needed.

It is noteworthy that American workers devoted little attention to the problem of the structure of the protein molecule, whereas European chemists centered their interest on this phase of protein chemistry. If the writer has not overlooked some important contributions in this field, the work in this direction was limited to that of Levene and Pfaltz,[7] and that of Carpenter. The former is concerned with the problem of the presence of ketopiperazine compounds in the protein molecule. These authors have made the observation that *d*-alanyl-*d*-alanine anhydride is readily racemized by the action of weak alkali, whereas *d*-alanyl-*d*-alanine is not. If rapid racemization under the influence of alkali should be found to be a general property of ketopiperazines, then by the

[2] J. Biol. Chem., **64**: 673; 1925.
[3] J. Am. Chem. Soc., **47**: 412; 1925.
[4] J. Biol. Chem., **66**: 475; 1925.
[5] J. Biol. Chem., **64**: 29; 1925.
[6] J. Am. Chem. Soc., **47**: 580; 1925.
[7] J. Biol. Chem., **68**: 277; 1925. J. Gen. Physiol., **8**: 183; 1925.

action of alkali on proteins one could obtain an indication of the presence or absence of cyclic compounds in the protein molecule.

In the course of the past year Levene and Pfaltz reported on the racemization of two ketopiperazines, levo-alanyl-glycine anhydride, on levo-prolyl-glycine anhydride and on the peptides glycyl-levo-alanyl-glycine and on diglycyl-levo-alanyl-glycine. The earlier observation was confirmed that ketopiperazines exposed to action of alkali for 48 hours racemized to the extent of 70% to 80% whereas the peptides had a maximum racemization of 7%. The work is being continued and final conclusions are not as yet forthcoming.

Another investigation dealing with the structural properties of proteins is that of Carpenter,[8] which is concerned with the influence of hydrogen ion concentration on the hydrolysis of casein. Carpenter found that on the acid side of the isoelectric point the hydrolysis follows a monomolecular reaction. On the alkaline side the reaction proceeds irregularly. Carpenter assumes that the irregularity is due to the fact that on the alkaline side there exist two tautomeric forms of casein, one below p_H 9, which is the salt of the ketonic form of CONH groups, and the other above p_H 9, having the enolic structure. The latter is the less stable form. There are some points of contact between the work of Carpenter and that of Levene and Pfaltz. The latter authors regard racemization as a result of enolization and they find that racemization of tri- and tetrapeptides is enhanced by increase in concentration of the alkali. Hence, increase in concentration of hydroxyl ions is favorable to enolization. The only difference in the two views is that Levene and Pfaltz, as Dakin did before them assume enolization of the following type:

$$\begin{array}{l} NH_2 \\ | \\ RCH-CONHR \end{array} \rightarrow \begin{array}{l} NH_2 \\ | \\ RC=C(OH)NHR \end{array}$$

Much more work in correlating chemical structure and properties of synthetic peptides, ketopiperazines and other derivatives is very much needed in order that the structure of the protein molecule may be revealed.

Methods of Physical Chemistry.

The progress made in the chemistry of proteins in course of last year by physical methods is less striking than that of the

[8] J. Biol. Chem., 67: 647; 1926.

immediately preceding years. Nevertheless, a few very important contributions have been reported. The most noteworthy of them deal with the combination of proteins and salts. The question of complex salt formation of proteins with the ions of electrolytes has engaged the interest of the protein chemists and of the biologists for a long time. In 1924 Northrop and Kunitz [9] came to the conclusion that Ca, Mg, K and Zn form complex salts with proteins. The principle of the method which led to this conclusion was the following: A solution of a protein and electrolyte was placed in a collodion bag which was immersed in a solution of the electrolyte. The solution was allowed to come to an equilibrium. The concentration in the bag of the selected ion was determined analytically. The ratio of the activities of the same ion within and without the bag was calculated by the Donnan equilibrium equation from the ratio of the activities of any diffusible ion within and without the bag determined potentiometrically. In the past year a very important simplification of the method was introduced by the same authors. Instead of measuring the ratio of the activities of the desired ion by the concentration cell method, it was calculated according to the Donnan equation from the membrane potential measurements. If ionic distribution ratio is given by the expression $r = \frac{Mo}{Mi}$, then the concentration of the combined ions is found from the equation $Mc = M_I - \frac{Mo}{r}$ where M_I is the total concentration of the ion inside and Mo is the total concentration of the ion outside. Robert F. Loeb [10] comes to a similar conclusion regarding the combination of the Ca ions with several proteins and with blood serum. The effect of the variations in concentrations of the salt ($CaCl_2$) and the protein and of the variation in the p_H was observed. The ratio $\frac{\text{Ca inside}}{\text{Ca outside}}$ in a general way agreed with that required by the Donnan equation. Some deviation, however, was observed which could be explained on the assumption of formation of a complex Ca-protein ion.

A similar conclusion was reached by David M. Greenberg and Carl L. A. Schmidt,[11] who observed the cataphoresis of casein

[9] J. Gen. Physiol., 9: 1387; 1926.
[10] J. Gen. Physiol., 8: 451; 1925.
[11] J. Gen. Physiol., 8: 271; 1926.

in solutions containing elements of alkali earths. The casein seemed to combine with a part of the metal ion to form complex ions moving in opposite directions to the path of the cation.

These very interesting observations will be of great importance in connection with many problems of biology and of other branches of applied protein chemistry. The structural chemistry of proteins will benefit by it in a lesser degree, inasmuch as it was shown by Pfeiffer that both amino acids and ketopiperazines are capable of forming complex salts with the ions of electrolytes and inasmuch as the point of disagreement regarding the structure of the protein molecule is the question whether proteins are to be regarded as complex amino acids or complex ketopiperazines.

Another important contribution to the physical chemistry of proteins is that by Northrop and Kunitz [12] on the swelling of gelatin in salt solutions. The authors measured the influence of salt on the osmotic pressure and on the swelling of gelatin. The experiments were performed at the isoelectric point of gelatin. The osmotic pressure was measured at 37° C and the swelling at 0° C. Under these conditions, they noted that the rise in osmotic pressure was accompanied by a parallel increase in swelling. There was also noted the formation of a non-diffusible ion of the protein with one of the salt ions leading to a Donnan equilibrium. However, the increase in osmotic pressure calculated from the Donnan equilibrium was lower than the observed, and the authors concluded that the swelling of gelatin in a salt solution is an osmotic phenomenon, though different from that established in the protein in a solution of acids. In the former case, the phenomenon is produced, not by diffusible ions, but by the gelatin itself.

Other work by the physical method was concerned with the determinations of what may be termed the physical constants of individual proteins. Noteworthy in this connection are the investigations of Tague [13] on the isoelectric points of gliadin and glutein and of Csonka, Murphy and D. B. Jones,[14] who determined the isoelectric points of a large number of proteins by the solubility method. It must be borne in mind, however, that all determinations of the physical constants of proteins may be regarded as provisional only, inasmuch as with few exceptions one has no assurance of the purity of the proteins. Even crystallization offers no sufficient guaranty of purity.

[12] J. Gen. Physiol., **8**: 317; 1926.
[13] J. Am. Chem. Soc., **47**: 418; 1925.
[14] J. Am. Chem. Soc., **48**: 763; 1926.

Biological Method. It is characteristic of proteins even more than of carbohydrates that some of their structural individualities can be discovered by methods of a biological nature. Some important contributions in this respect have been made in the course of the past year. Of these the one by Sherman and Woods has already been referred to. In this place mention should be made of the work of Julia H. Lewis and H. Gideon Wells on the immunological relationship of several alcohol soluble vegetable proteins. More extensive work in this direction is much desired

Chapter XXIII.

Nucleic Acids.

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The work on nucleic acids in the past year centred on several fundamental points of structure. The investigations were concerned principally with the structure of plant nucleic acid and of a nucleic acid isolated from a bacterium, the *B. subtilis*.

Since the publications of Levene, followed by some detailed work of Levene and Jacobs, plant nucleic acid has been regarded as a mononucleotide. After some dispute the theory of Levene was generally accepted, though there remained a disagreement as to the mode of linkage between the individual nucleotides. According to Levene, the individual nucleotides are joined through an ester union, whereas Jones suggested an ether linkage between the sugars of each nucleotide. Later Jones modified his view, holding the question of ether linkage in one unit, admitting two ester linkages.

Last year Jones and Perkins[1] published an article in which they radically changed their conception of the size of the nucleic acid molecule. They have assumed that plant nucleic acid is composed of only three nucleotides, namely, of adenosine, guanosine and cytidine phosphoric acids and that adenine phosphoric acid is a product of hydrolysis of cytidine phosphoric acid. In the past the identical disagreement with Levene's conception was expressed by Steudel and his co-workers (Levene[2]). The latter authors, however, have accepted the mononucleotide theory. Jones[3] has advanced several theoretical arguments against the view of Jones' splitting and has, thus would and cytidine are obtained in equimolecular proportions on hydrolysis of plant nucleic acid, whereas

[1] *Biol. Chem.*, 42, 227 (1920).
[2] *Biol. Chem.*, 42, 227 (1920).

animal nucleic acid yields under identical conditions only a minimal proportion of uracil. Furthermore, it should be expected that in cytidine phosphoric acid the phosphoric acid radical should be more readily hydrolyzable than the amino group. Indeed, he showed experimentally that cytidine phosphoric acid dissolved in a 5% solution of ammonium hydroxide remains unchanged, whereas nucleic acid subjected to the same treatment yields uridine phosphoric acid, thus substantiating the tetranucleotide theory.

In a paper by Levene and Simms,[3] evidence was advanced in favor of the ether-linkage between the individual nucleotides. The argument is the following: The molecule of nucleic acid built according to the theory of Levene contains four primary phosphoric acid groups and one secondary; the one built according to the older theory of Jones contains four primary and four secondary, and the one according to the newer theory of Jones contains four primary and two secondary. Thus, a choice of one of the three alternative structures depends on an accurate estimation of the number of secondary phosphoric acid groups present in the nucleic acid molecule. Levene and Simms have studied the dissociation constants of nucleosides, nucleotides and nucleic acids. The phenolic and the basic dissociation constants of the pentosides were determined on the first; the phosphoric acid dissociation constants of the simple nucleotides were then determined. From these data the dissociation constants of the phosphoric acid groups of nucleic acids were roughly calculated. These values were then compared with those determined experimentally on samples of nucleic acid. The secondary phosphoric acid dissociation constants should lie between p_H 4.5 and p_H 9. In this range the molecules of Jones should bind 4 or 2 equivalents of alkali; that assumed by Levene, only one equivalent. The experimental data agree with the theory of Levene. One, however, must bear in mind that nucleic acids are amorphous colloidal substances and further work on the purification of nucleic acids is much desired in order that the physicochemical evidence can be fully relied upon.

Also the mode of union of the component elements of nucleosides was again discussed in the course of the past year. Levene had previously methylated xanthosine and through this process converted it into theophylline riboside (1,3-dimethylxanthine

[3] J. Biol. Chem., 65: 519; 1925.

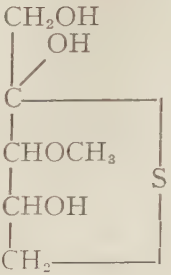
riboside) and had concluded that the sugar rest was attached to a nitrogen atom of the imidazole ring. Levene and Sobotka [4] have now prepared the theophylline riboside synthetically and found it identical with the one previously described by Levene. They have also prepared a xyloside of the same base. Levene and Sobotka [4] have also synthesized pentosides of substituted uracils in order to study the influence of position of the sugar on the rate of hydrolysis with the view of finding a basis for determining the position of the sugar in the natural pyrimidine ribosides. They found that the pyrimidines in the synthetic pentosides functioned principally in the enolic form, and therefore were much less stable than the natural pyrimidine pentosides. This concludes the list of publications dealing with the structure of the plant nucleic acid. However, in connection with the work on plant nucleic acid mention must be made of a very noteworthy paper by H. O. Calvery,[5] in which the isolation of an adenine nucleoside from tea leaves is described.

The most exciting announcement in the field of nucleic acid chemistry, however, is the report of T. B. Johnson and R. D. Coghill [6] on the isolation of a new base, methylcytosine (2-hydroxy-5-methyl-6-aminopyrimidine) from tuberculinic acid (the nucleic acid of *B. tuberculosis*). The announcement, however, has the character of a preliminary report. The work of Johnson and his co-workers on tuberculinic acid promises to be very important in many respects, but discussion of the work should be postponed until he will have had time to prepare a sufficient quantity of truly pure tuberculinic acid and will have had the chance to work on the structure of the purified material.

Since the work on nucleic acids embraces also that of nucleosides, mention may be made in this place of the work on a thionucleoside. The substance was isolated first in 1912 by J. A. Mandel and E. K. Dunham.[7] The conclusion of these authors regarding the nature of the sugar was erroneous. Later Levene demonstrated that the sugar, though having the composition of a hexose, was different from all known hexoses. Then Suzuki, Odake and Mori [8] made the remarkable discovery that the sugar of the new nucleoside contained sulfur and was a methylthiopen-

[4] J. Biol. Chem., **65**: 463, 469; 1925.
[5] J. Biol. Chem., **68**: 593; 1926.
[6] J. Am. Chem. Soc., **47**: 184; 1925.
[7] J. Biol. Chem., **11**: 851; 1912.
[8] Biochem. Z., **154**: 278; 1924.

tose. Levene and Sobotka [9] suggested for the sugar one of the following two structures:



Finally, all those engaged in work on nucleic acids may be interested in the communication of O. Baudisch and D. Davidson [10] on the oxidation of thymine. This work confirms the view previously expressed by Baudisch and Bass that the formation of thymine glycol is the first phase in such oxidations of thymine, the final product of which is pyruvic acid.

[9] J. Biol. Chem., **55**: 551; 1925.
[10] J. Biol. Chem., **64**: 233; 1925.

Chapter XXIV.

Rubber.

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Research work on rubber in its scientific and industrial aspects has continued to attract the attention of chemists throughout the world. In Europe such work as has been published has come largely from scientific and university circles, while in this country the laboratories connected with the industries have furnished a majority of the papers. One never can be quite sure, therefore, to what extent the published papers reflect the real progress of the science in the United States. And, as is natural under such conditions, our chemists lean in their publications toward the applied aspects of rubber chemistry.

There has, nevertheless, been considerable work done on the fundamental properties of the rubber hydrocarbon, in which field Fisher [1] has continued his studies of the reactivity of rubber and finds the effect of various reagents on the chemical unsaturation and found that heat, in the absence of air, at temperatures around 141° C. causes no drop in chemical unsaturation but at 245° to 360° C. there is a lowering of unsaturation; trichloroacetic acid causes lowering; ultraviolet light causes none; mastication in the air causes lowering, but in carbon dioxide there is none.

Fisher, Gray and McColm [2] show Weber's tetroxyphenylpolyprene not to have the ether formula but the hydroxy structure $R(C_6H_4OH)_2$ and is rubber di[hydroxyphenyl].

In the field of synthetic rubber there has been no work done in this country although Weber,[3] a few months before his lamented death, published his opinions on the possibilities of commercial synthetic rubber and held out the belief that it would be difficult

[1] Fisher and Gray, Ind. Eng. Chem., 18: 414; 1926.
[2] J. Am. Chem. Soc., 48: 1309; 1926.
[3] Ind. Eng. Chem., 18: 404; 1926.

if not impossible of attainment. Various optimistic assertions regarding possible sources and the great need of synthetic rubber have flavored the meetings of the societies, however. Bruson,[4] joining with Staudinger in his title, wrote on some work done under Staudinger in Zürich, on cyclopentadiene rubber, a new cyclic synthetic polymerization product. The work is a significant study of polymerization catalysts. The results are interesting to the synthetist for the product is rubber-like, vulcanizable and sufficiently different from natural and the older synthetic rubbers to command serious attention.

The physical structure of dry crude rubber, and of the particle, or globule, of it as it is found in latex, which has commanded the attention of so many of our European friends, has been during the year the subject of some fundamental research. Sebrell, Park and Martin [5] have investigated under the microscope, the mechanism of the coagulation of latex and the structure of the coagulated rubber. They did some clever motion picture work in making a record of their observations. They verified some of the earlier theories and conclude rubber to be a closely packed mass of discrete latex globules, which structure persists after vulcanization. These data and the excellent microphotographs accompanying the article are significant for the rubber technologist.

Green,[6] just prior to the paper above mentioned, has shown some photographs of latex globules in the attempt to solve the problem of the ultimate condition of sulfur in vulcanized rubber. His paper is a study of a method of attack and should be of value to those who have microscopic facilities, for the problem of vulcanization is yet far from solved, or in any event the several theories are far from universal acceptance. His paper has much of value on the structure of rubber.

The globules of rubber in latex have long been known to carry a negative electric charge, a fact which has been taken in hand by Sheppard and Eberlin,[7] who have developed a technique by which they deposit rubber and rubber mixtures on an anode by electrolytic methods. Various mixtures were used and they were subsequently vulcanized.

Although the number of organic accelerators of vulcanization is legion, this field still has some attention. Dinsmore and Zimmer-

[4] Ind. Eng. Chem., 18: 381; 1926.
[5] Ind. Eng. Chem., 17: 1173; 1925.
[6] Ind. Eng. Chem., 17: 802; 1925.
[7] Eng. Chem., 17: 711; 1925.

man [8] have run systematic tests on rubber with and without accelerators in order to arrive at a basis for judgment of the quality of the vulcanized composition. They believe that an accurate judgment of quality can be reached by the aid of three criteria, namely, rate of cure, rigidity, and resistance to tearing (at the best cure). Our English friends have taken exception to certain of the conclusions, and one may expect more work along the line of what constitutes a correctly cured composition. This field is fundamentally that of the principles of vulcanization, one which although it has been ploughed vigorously, still needs the removal of many rocks before we can be confident of its character.

The vulcanization of hard rubber has been attacked by Glancy, Wright and Oon,[9] who show the action of accelerators on the coefficient of vulcanization of typical hard rubber compositions. Accelerators simply hasten the rate of sulfur combination and do not give additional strength as is the case in soft rubber.

The properties of vulcanized rubber must ever have a prominent place in the research program of industrial laboratories, and although little of the work is chemical, in the strict sense, reference to it should not be overlooked. Wiegand [10] has advanced further work along the line of the energy criteria and the stress-strain curve, as these are influenced by different mineral substances in the rubber mixture.

A thoroughly scientific paper on the electrical properties of raw rubber, vulcanized rubber and gutta percha has been presented by Curtis and McPherson,[11] who have exhaustively measured the dielectric constant, power factor and resistivity of these substances under various conditions. This study is of especial value to those interested in the wire and cable industries. The absorption of water by rubber did not reach an equilibrium and was as high as 5-40%.

Boggs and Blake,[12] also, find rubber a good absorbent for water, indeed at times up to 500%, and they believe that the absorption is largely due to non-rubber constituents of the crude material. Closely related to the absorption of water by rubber are the observations of Stringfield,[13] who studied the effect of humidity

[8] Ind. Eng. Chem., **18**: 144; 1926.
[9] Ind. Eng. Chem., **18**: 73; 1926.
[10] Ind. Eng. Chem., **17**: 623, 939; 1925. Indian Rubber J., **70**: 900, 933; 1925.
[11] Bur. Standards, Tech. Paper No. 299; 1925.
[12] Ind. Eng. Chem., **18**: 224; 1926.
[13] Ind. Eng. Chem., **17**: 833; 1925.

to which rubber is exposed before and after vulcanization, and its effect on the physical testing of rubber. A fairly constant (40-60%) relative humidity must be maintained in order to obtain concordant results in tensile strength and other physical properties.

The action of dry powders in rubber mixtures has had some attention. Cranor [14] studied the stiffening effect of zinc oxide and several varieties of carbon black at different volumes in rubber mixtures and drew conclusions favorable to carbon black.

Spear and Moore [15] made a microscopic study of the distribution of carbon black in rubber mixtures but come to no very clear conclusions. In a later paper [16] they discuss the stiffening effect of carbon black without reaching a stopping point, except to remark upon the already well-known fact, that fineness of subdivision of the particles plays a part.

Thies [17] worked on clays in an attempt to find a test to apply to determine good clays and bad ones without vulcanizing them in test mixtures. He found that all clays absorb dyes and that those good in rubber mixtures absorb less dyes than those that are bad.

Aging tests to be applied upon vulcanized rubber in order to predetermine the life of the mixtures under normal conditions came up for an extended discussion at one of the meetings of the American Chemical Society. Three methods of accelerated aging test were mentioned, namely, the oxygen bomb test of Bierer-Davis, the air oven test of Geer and the oxygen oven test of Bruni and Marzetti. Bierer and Davis [18] described their test in detail as an extension of their earlier presentation.[19] They conclude the test to be reliable as an index of natural aging. Morron and Webster [20] agree. Rushee [*ibid.* 868] and Thomson [*ibid.* 868] concur but mention the danger from explosion. Sommerville [*ibid.* 869] inclines toward the Bruni and Marzetti oxygen oven method. Glancy [*ibid.* 869] believes that the Bierer and Geer methods agree pretty well on high-grade stocks. Vogt [*ibid.* 870] found all tests misleading and irregular. Winkelmann [*ibid.* 871] and Jones [*ibid.* 871] show what is more interesting from a scientific standpoint, that decay of vulcanized rubber on

[14] India Rubber J., 70: 63; 1925.
[15] Ind. Eng. Chem., 17: 936; 1925.
[16] Ind. Eng. Chem., 18: 418; 1926.
[17] Ind. Eng. Chem., 17: 1165; 1925.
[18] Ind. Eng. Chem., 17: 860; 1925.
[19] Ind. Eng. Chem., 16: 711; 1924.
[20] Ind. Eng. Chem., 17: 866; 1925.

standing is due to an oxidation reaction. The effect of light on vulcanized rubber was expounded by Williams,[21] who concluded that light catalyzes oxidation, and that short waves were more effective in producing surface oxidation. Ozone is the active cause of surface cracking but is not effective unless the sample be stretched. Along this line the work of Haushalter [22] is interesting. He observed the effect of corona on stretched and unstretched rubber, and found that unstretched rubber was but little affected. Jecusco [23] added light to an aging oven and found some interesting data but could draw no final conclusion. By the method of impact strength tests Dieterich and Gray [24] found hard rubber to show relatively little change due to aging at 158° F, but at 300° F the deterioration was rapid. Age retarders showed slight effect.

Shepard, Krall and Morris [25] exposed samples of many rubber mixtures to the weathering action of sunlight in the open air and found the effect of several ingredients in hindering the deterioration.

The past year has been full of argument with respect to the so-called rubber monopoly and so the chemists stepped in to elucidate the value of reclaimed rubber to the industry. Holt and Wormeley [26] have indicated that the wearing quality of tire treads is reduced by the substitution of reclaimed rubber for new natural rubber in a given set of tire tread formulas. On the other hand, Bierer and Davis,[27] in a not too convincing presentation, claim that reclaimed rubber can be used to replace considerable volumes of crude even in tire treads, provided the changes in the mixture are made intelligently, and rubber be not merely substituted by reclaimed.

Research Problems.

Research problems in the field of rubber chemistry have had but little attention in the university centers, perhaps due to the need of vulcanization and physical test as the final proof of value. Such testing requires some small machinery. If, however, chemists would realize that such machinery is simple and not expensive, they may be led into studies in a field at once fasci-

[21] Ind. Eng. Chem., 18: 367; 1926.
[22] Elec. World, 86: 267; 1925. India Rubber J., 70: 897; 1925.
[23] Ind. Eng. Chem., 18: 420; 1926.
[24] Ind. Eng. Chem., 18: 428; 1926.
[25] Ind. Eng. Chem., 18: 615; 1926.
[26] Bur. Standards, Tech. Paper No. 294; 1925.
[27] Ind. Eng. Chem., 18: 348; 1926.

nating because of its complexity and possibly productive on account of its industrial applications. Let me remark as a suggestion to any who may take up such studies for the first time that they test or vulcanize new materials only in well standardized simple formulas.

The following are a few of the many problems upon which light is needed.

1. A precise determination of the Joule effect by modern methods and upon standard mixtures.
2. What is the precise part played by different dry mineral powders in the rubber mixture? We know the effect pretty well but not the cause.
3. Studies in abrasion. Why do different compositions wear away at different rates?
4. The composition of the latex particle along the line of Hauser's work should be undertaken with especial reference to the effect of mastication upon structure. A good deal of work has been done but more is needed in order to reach final conclusions.
5. The X-ray studies of structure are significant but are disputed in certain circles. A more extended study would be worth while.
6. A major problem is to answer the question, Why is rubber elastic? Is there an elastic structure of the rubber molecule?
7. Polymerization catalysts of isoprene and butadiene into rubber would throw light on the chemical nature of rubber.
8. The problem of oxidation of vulcanized rubber needs study and accelerated aging tests need to be brought to a scientific basis.
9. The theory of vulcanization is an ever present problem of vast extent and with many ramifications.
10. The physical constants of crude rubber and of typical mixtures would add to our knowledge.
11. Allied to the theory of vulcanization is the reversal of it. Can sulfur be removed? It is the reclaiming problem in its scientific aspects.

Chapter XXV.

Cellulose.

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While great advances have been made in America in the technical application of cellulose and its derivatives, a review of the literature indicates that the major portion of the published results have appeared in foreign journals.

Much work has been done on the X-ray spectra of cellulose and its modifications. Probably the most important is that of R. O. Herzog,[1] in which he has shown that the unit cell must consist of 1, 2, or $4C_6H_{10}O_5$ groups. He points out that n in $(C_6H_{10}O_5)_n$ may be indefinitely great, but that the values 3 and 5 for n are excluded. J. R. Katz,[2] in a theoretical discussion, states that the cellulose molecules may actually be larger than the elementary cells or units that are indicated by the Roentgen spectrographic methods. He further points out that the size of the aggregate may be determined by the residual valency existing between the unit cells. Changes in X-ray spectrum upon mercerization have been investigated by Katz.[3] He finds that new spectral lines appear at approximately identical places independent of the alkali metal hydroxide used. This points to a structural change. After washing, the original cellulose spectrum is obtained with the lattice somewhat enlarged and a new band present. He found that the breaks in Heuser's [4] alkali adsorption curves occur at the same concentrations as the disappearances of the original cellulose spectra. Cotton and wood pulps, according to Herzog,[5] give identical X-ray diagrams, while films of cellulose nitrate show no crystalline structure.

* With the coöperation of Cyril J. Staud.
[1] Cellulosechemie, **6**: 39; 1925.
[2] Cellulosechemie, **6**: 37; 1925.
[3] Cellulosechemie, **6**: 35; 1925.
[4] Cellulosechemie, **6**: 13; 1925.
[5] Papierfabr., **23**: 121; 1925.

From data obtained from cellulose cuprammonium solutions, Hess concluded that the molecule of cellulose is $(C_6H_{10}O_5)_1$. Bauer [6] considers that the data fit equally well when substituted in the Freundlich adsorption equation, and that the phenomenon is one of peptization.

Another view of the nature of the cuprammonium solution of cellulose is presented by S. M. Neale,[7] who puts forward the hypothesis that such a solution is a colloidal electrolyte of the type of soap solutions.

Hess and his co-workers [8] have shown by the acetolysis of cellulose, that celloisobiose octaacetate may be obtained without hydrolyzing to the carbohydrate. Since celloisobiose octaacetate does not yield cellobiose octaacetate on treatment with acetic anhydride and sulfuric acid, as does celloisobiose, they assume that the cellobiose linkage is not pre-formed in cellulose. They failed to find any evidence of the existence of the trisaccharide "Procellose" of Bertrand and Benoist.[9]

Heuser and Hiemer [10] claim to have measured the degree of depolymerization of cellulose degraded by different treatments. This was done by determining the molecular weight of the dimethyl derivative and dividing by 190, the molecular weight of $C_6H_8O_3(OCH_3)_2$.

Hess [11] questions the conclusions of Heuser on the ground that the products of the methylation were impure.

In investigating the degree of dispersion or depolymerization of cellulose, Herzog and Krüger [12] have found that cellulose acetate disperses in acetone when the particle diameter is less than 20 μμ.

Attention must be called to the voluminous papers of von Veimarn [13] on the dispersoidology of cellulose, which are too extensive to permit of review.

Much work has been done on the action of alkali hydroxides on cellulose. D'Ans and Jaeger [14] studied the data given by several workers and by combining these with their results, arrived at some interesting conclusions. Among these is the con-

[6] Kolloid-Z., 36: 257; 1925.
[7] J. Textile Inst., 16: 363-369T; 1925.
[8] Ann., 443: 71; 1925.
[9] Bull. soc. chim. (4), 33: 1451; 1923.
[10] Cellulosechemie, 6: 101, 125, 153; 1925.
[11] Z. Elektrochem., 31: 613; 1925.
[12] Naturwissenschaften, 13: 1040; 1925.
[13] Reports Imp. Ind. Research Inst., Osaka, Japan, 5; No. 18: 7, 189; 6; No. 10: 11; 1925.
[14] Cellulosechemie, 6: 137; 1925.

centration of sodium hydroxide (12%) at which maximum solubility of cellulose takes place.

A review of the alkali cellulose situation is given by Voss [15] with fifty-five references.

The nature of hydro and oxidized cellulose has been further elucidated by Hibbert and Parsons,[16] Hess,[17] Knecht and Müller [18] and Karrer and Lieser.[19] Hibbert and Parsons regard oxidized cellulose as a mixture of partly depolymerized cellulose with small quantities of complex oxidation products which show aldehydic and acidic properties. Hess considers hydrocellulose to be a mixture containing a physically changed cellulose analogous to cellulose A, and cellulose dextrin and oxidized cellulose to be probably a mixture of cellulose A with decomposition products soluble in the oxidizing solution. Karrer and Lieser state that hydrocellulose, if properly made, may be distinguished from oxidized cellulose by its low acidity and that upon heating with calcium hydroxide no isosaccharinic acid is formed, thus resembling cellulose rather than oxidized cellulose.

Crystalline cellulose acetate has been prepared by Hess, Schultze and Messmer.[20] Saponification of these crystalline derivatives gave a substance which upon solution in cuprammonium gave the same optical rotation as cellulose.

Nierenstein [21] reports a partial methylation of cellulose by the use of diazomethane.

That the ripening of viscose is accompanied by a chemical change is emphasized by deWyss [22] who found that Leuch's [23] method of analysis is erroneous. deWyss found that the proportion of xanthate sulfur to cellulose fell more than 50% in 160 hours. He also found that the change in composition of the cellulose xanthate bears a definite relation to the ease of coagulation of the viscose. Morse [24] describes a process of making viscose in the laboratory.

Apparent errors in the method as given by Schwalbe have led various workers to investigate the copper number procedure.

[15] Kunstoffe, **15**: 192; 1925.
[16] J. Soc. Chem. Ind., **44**: 473; 1925
[17] Papierfabr., **23**: 122, 164; 1925.
[18] J. Soc. Dyers Colourists, **43**: 46; 1925.
[19] Cellulosechemie, **7**: 1; 1926.
[20] Ann., **444**: 266; 1925.
[21] Ber., **58B**: 2615; 1925.
[22] Ind. Eng. Chem., **17**: 1043; 1925.
[23] Chem. Ztg., **47**: 801; 1923.
[24] Ind. Eng. Chem., **18**: 398; 1926.

Bray and Liu [25] recommend a technique which they believe to be superior to that of Schwalbe. Griffin [26] recommends the method of Braidy. Staud and Gray [27] found that a minimum blank could be obtained with a modified Fehling solution. They further observed that the copper number is a function of the temperature at which the determination is made and that the temperature coefficient is different for pulp than for cotton. They also showed that the time-copper number curve becomes horizontal at 30 minutes' heating and for this reason selected 45 minutes as the minimum time of heating.

Parsons [28] discusses the significance of the alpha-cellulose determination and the necessity of further work on this subject. He records concordant results using the method of Jentgen, with modifications.

A report of the German Fiber Analysis Commission's findings is given by Schwalbe,[29] who states that the Jentgen method gave the highest and most concordant results, while the Waentig procedure gave the lowest and most deviating values and the method proposed by the Commission fell between these two. They recommend a procedure which is a compromise between the Jentgen and one of the modified methods.

The ash content and ash alkalinity of cottons from various sources were determined by Fargher and Probert.[30]

Hess [31] finds that celluloses from various sources exhibit the same optical rotation in cuprammonium solutions, thus enabling cellulose to be differentiated from other polysaccharides.

The yield values of films made from cellulose esters have been studied by Sheppard, Carver and Sweet,[32] who have found that the yield points as obtained on strength testing machines vary with the speed at which the machine is run.

There is great need of intensive research on cellulose by American workers on the purely theoretical side.

Today we have a so-called standard cellulose made from long fibered cotton, but the criteria of its purity are very slight and insufficient. It is of importance to ascertain whether the fiber is homogeneous, that is, of uniform chemical composition through-

[25] Paper Trade J., 80, No. 22: 49; 1925.
[26] Paper Trade J., 82, No. 8: 150; 1926.
[27] Ind. Eng. Chem., 17: 741; 1925.
[28] Paper Trade J., 82, No. 8: 211; 1926.
[29] Papierfabr., 23: 697; 1925.
[30] J. Textile Inst., 17: 46T; 1925.
[31] Ann., 444: 287; 1925.
[32] Ind. Eng. Chem., 18: 76; 1926.

out, or whether the cuticle and lining of the lumen are of different composition. Possibly the difference is merely in the physical structure.

We do not know whether celluloses from various sources differ chemically or physically or both. Methods of establishing the identity or lack of identity from a chemical standpoint are highly desirable.

Another problem is, how does cellulose exist in wood? Is it in chemical combination with the lignin or sugar anhydrides or is it uncombined? Another question in connection with this is, how much is the cellulose changed by the methods now employed to isolate it?

Important data concerning some of the above problems may be obtained by studying the X-ray spectra of cellulose from various sources and derivatives of the same. The question of the constitution of cellulose may be helped by a study of the products obtained by very carefully regulated oxidations of cellulose as recommended by Hibbert and Parsons.

There is need of new analytical methods to serve as criteria of purity, and for differentiating various celluloses as used in the arts.

The copper number as used at present fails to give the true reducing value of the cellulose. A new method employing acid solutions is very desirable.

These represent but a few of the problems upon which work might profitably be done.

Chapter XXVI.

Sugar Chemistry.

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The researches will be reviewed under the general classification of (1) analytical methods, (2) the occurrence and preparation of sugars, (3) the oxidation of sugars, including their metabolism, (4) the action of enzymes on sugars, and (5) studies relating to the structures of the sugars.

Analytical Methods.

Several researches having for their purpose the increase of accuracy in the determination of reducing sugars in blood, urine, cerebrospinal fluid, etc., have appeared during the year.[1] A method for the estimation of glucosan in the urine, by converting it to glucose through acid hydrolysis, has been devised.[2] References concerning in part the analysis of constituents of pectin will be found in the second section of this report. Collaborative tests of several analytical sugar methods by members of the Association of Official Agricultural Chemists are published in the reports of that association.[3] The designation by Zerban of the method for determining raffinose and sucrose in

[1] Sumner, J. Biol. Chem., **65**: 393; 1925. A more specific reagent for the determination of sugar in urine. Harned, J. Biol. Chem., **65**: 555; 1925. The sugar content of blood. Benedict, J. Biol. Chem., **68**: 759; 1926. **64**: 207; 1925. The estimation of sugar in blood and normal urine. Lyttle and Hearn, J. Biol. Chem., **68**: 751; 1926. A comparison of the Folin-Wu and the new Benedict method for sugar in blood and cerebrospinal fluid. Folin, J. Biol. Chem., **67**: 357; 1926. The determination of sugar in blood and in normal urine. Quick, Ind. Eng. Chem., **17**: 729; 1925. Effect of sodium carbonate concentration in the Benedict sugar method. Campbell, J. Biol. Chem., **67**: 59; 1926. The quantitative determination of dihydroxyacetone. Duggan and Scott, J. Biol. Chem., **67**: 287; 1926. A critical examination of four methods commonly used for the determination of sugar in blood. Oser and Karr, J. Biol. Chem., **67**: 319; 1926. The correction of Folin-Wu blood sugar values.

[2] Deuel, Waddell, and Mandel, J. Biol. Chem., **68**: 801; 1926.

[3] Schneller, J. Assoc. Official Agr. Chem., **9**: 156; 1926. Drying, densimetric and refractometric methods. Zerban, J. Assoc. Official Agr. Chem., **9**: 166; 1926. Polariscopic methods. Jackson, J. Assoc. Official Agr. Chem., **9**: 178; 1926. Chemical methods for reducing sugars

admixture by use of the enzymes invertase and melibiase as the "two enzyme method of Paine and Balch" [4] and the official adoption of the method under this name by the Association leads the reviewer to record that this method in its essential principles was devised some years ago by Hudson and Harding.[5] Paine and Balch have adapted it to the simultaneous estimation of raffinose and sucrose in beet products but there is nothing novel in the principles upon which their directions are based. Von Lippmann [6] has likewise disputed the originality claimed by Paine and Balch.

The Occurrence and Preparation of Sugars.

Anderson and Sands [7] have discovered an excellent new source for the preparation of *l*-arabinose. Yields of 27% to 36% crystalline sugar were obtained by the acid hydrolysis of the gum from the mesquite tree (*Prosopis juliflora*) of the southwestern United States and Mexico. Certain simplifications in the preparation of raffinose from cottonseed meal, which remains the best known source for this trisaccharide, have been recommended.[8] Berlin [9] has identified gentiobiose by means of its crystalline β-octaacetate as one of the condensation products that result from the action of acid solutions upon *d*-glucose and expresses the opinion that the osazone which Emil Fisher obtained from such a mixture and named isomaltose osazone was impure gentiobiose osazone. The definition of "isomaltose" must apparently therefore be revised. From the mother liquors of the preparation of chloroheptaacetyl lactose Hudson and Kunz [10] have isolated an isomeric crystalline substance which is reported to be the chloroheptaacetate of a new disaccharide, having the structure *d*-galactosido-*d*-altrose. The new disaccharide has been named *neolactose*. By a similar reaction Hudson [11] has obtained from cellobiose octaacetate the crystalline chloroheptaacetate of another new disaccharide, to which the name *celtrobiose* has been given.

Several articles pertaining to the chemical technology of sucrose and sirup manufacture may be mentioned by title.[12]

[4] Paine and Balch, Ind. Eng. Chem., 17: 240; 1925.
[5] Hudson and Harding, J. Am. Chem. Soc., 37: 2193; 1915.
[6] Von Lippmann, Deut. Zuckerind., 51: 375; 1926.
[7] Anderson and Sands, Ind. Eng. Chem., 17: 1257; 1925. Mesquite and some other gums are described by Anderson, Sands and Sturgis, Am. J. Pharm., 97: 589; 1925.
[8] Englis, Decker, and Adams, J. Am. Chem. Soc., 47: 2724; 1925.
[9] Berlin, J. Am. Chem. Soc., 48: 1107; 1926.
[10] Hudson and Kunz, J. Am. Chem. Soc., 47: 2052; 1925.
[11] Hudson, Ind. Eng. Chem., 18: 633; 1926.
[12] Knowles, "Soft sugar color standards." Ind. Eng. Chem., 17: 980; 1925. "Tem-

An extensive paper[13] describing the preparation of fructose from various sources, and particularly from the Jerusalem artichoke and the dahlia, shows that it can be made from these plants at very moderate cost. Its crystallization has been successfully performed from aqueous solution. A bulletin[14] has been issued giving thorough details of recommended methods for making sugar-cane sirups. The authors have neglected to state the reference to the earlier article of Dale and Hudson[14a] and their remark that the application of invertase to sirup manufacture was only "suggested" by Dale and Hudson is erroneous. The making of cane sirup by this process was fully worked out by Dale and Hudson.

Several articles dealing with the preparation, practical uses and analysis of pectin have appeared.[15] The presence of galacturonic acid, galactose and arabinose in the pectin from various plants seems fairly well established and it appears that the decomposition of galacturonic acid to furfural and carbon dioxide can be used as an analytical method for determining this constituent in the presence of the two sugars.[16]

Some theophylline pentosides and substituted uracil xylosides have been synthesized by Levene and Sobotka[17] in the course of the study of the naturally occurring nucleosides. In his studies of mucoproteins (*i.e.*, complex proteins containing carbohydrates in their molecule) Levene[18] has obtained evidence of the presence of chitosamine and galactose as constituents of the mucoproteins of snails. Levene and Simms[19] have measured the dissociation constants of some plant nucleotides and nucleosides

perature and analytical changes in sugar liquor during bone black filtration." Ind. Eng. Chem., **17**: 1151; 1925. Lindfors, "Physical examination of sugar juices." Ind. Eng. Chem., **17**: 1155; 1925. Bachler, "Subjection of molasses treated with zeolites to the Steffen's process." Ind. Eng. Chem., **18**: 180; 1926. Blowski and Bon, "Decolorizing Carbons." Ind. Eng. Chem., **18**: 32; 1926. Criticism by Wickenden and reply by the authors in Ind. Eng. Chem., **18**: 649; 1926. Snyder, "Temperature corrections to reading of Baumé hydrometers. Bureau of Standards Baumé scale for sugar solutions (standard at 20° C.)." U. S. Bureau of Standards, Circular No. 295.

[13] Jackson, Silsbee, and Proffit, Scientific Papers of the Bureau of Standards, No. 519; 1926.

[14] Paine and Walton, "Sugar-cane sirup manufacture." U. S. Dept. of Agriculture, Bulletin No. 1370.

[14a] Dale and Hudson, "Invertase process of manufacturing sirup." Am. Food J., **17**: 27; 1922.

[15] Wilson, "The manufacture of pectin." Ind. Eng. Chem., **17**: 1065; 1925. Jameson, "Requirements of pectin for the commercial jelly-maker." Ind. Eng. Chem., **17**: 1291; 1925. Baker, "Jelly strength of pectin jells." Ind. Eng. Chem., **18**: 89; 1926. Griggs and Johnstin, "Preparation and colloidal properties of pectin, preliminary report." Ind. Eng. Chem., **18**: 623; 1926. Ahmann and Hooker, "The determination of pectin, titration method." Ind. Eng. Chem., **18**: 412; 1926.

[16] Dore, J. Am. Chem. Soc., **48**: 232; 1926.

[17] Levene and Sobotka, J. Biol. Chem., **65**: 463, 469; 1925.

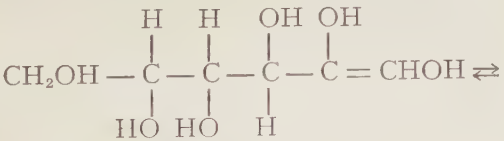
[18] Levene, J. Biol. Chem., **65**: 683; 1925.

[19] Levene and Simms, J. Biol. Chem., **65**: 519; 1925.

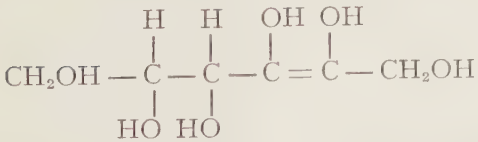
to obtain evidence regarding the mode of linkage of these substances in the nucleic acid structure. Levene and Sobotka [20] give new experimental data on the interesting thio sugar from yeast and discuss possible structures for it.

The Oxidation of Sugars.

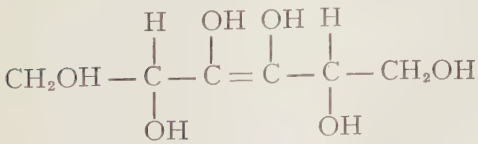
The theory which Nef proposed some years ago as a development of the Wohl-Neuberg enediol conception of sugar structures, to account for the various substances that result from the action of alkaline solutions on the reducing sugars has proved a very suggestive guide and many of its indications have been experimentally realized. In several articles on "the mechanism of carbohydrate oxidation" W. L. Evans and co-workers [21] have discussed various deductions from this theory and presented much new experimental evidence which supports it. It is assumed that in an alkaline solution of glucose, for example, there are formed the following 1-2, 2-3, and 3-4 enediols which are interconvertible, and that these substances in the presence of oxidizing agents undergo a splitting at the double bonds, thus giving rise to methylenenols of *d*-arabinose and formaldehyde (from the



d-Glucose, 1,2-enediol



d-Glucose, 2,3-enediol



d-Glucose, 3,4-enediol

[20] Levene and Sobotka, J. Biol. Chem., 65: 551; 1925.

[21] Evans, Buehler, Looker, Crawford, and Holl, J. Am. Chem. Soc., 47: 3085; 1925. Evans and Buehler, J. Am. Chem. Soc., 47: 3098; 1925. Evans and Holl, J. Am. Chem. Soc., 47: 3102; 1925.

1,2-enediol), *d*-erythrose and glycolic aldehyde (from the 2,3-enediol), and glyceric aldehyde (from the 3,4-enediol), and that these aldehydes then undergo oxidation, rearrangement, etc., in usual ways. Thus glyceric aldehyde can give rise in alkaline solution to lactic acid through the intermediate formation of pyruvic aldehyde, and gentle oxidation of the aldehydes first formed from the three enediols can yield *d*-arabonic, formic, *d*-erythronic, glycolic and glyceric acids. Nef has shown that these acids can indeed be isolated under conditions of mild alkaline oxidation of glucose. Power and Upson [22] have now obtained them from the oxidation of glucose at ordinary temperature (25-28°) by lime water and air, and they were likewise found by Jensen and Upson [23] from the oxidation of glucose by copper carbonate in sodium carbonate solution (Soldaini's reagent). Evans shows that the strong oxidizing action of permanganate on sugars in alkaline solution yields principally carbonic and oxalic acids and a trace of acetic acid. The carbonic acid apparently results from the oxidation of formic acid, while glycolic and glyceric acids yield oxalic acid. The relative proportions of carbonic and oxalic acids resulting from a given oxidation may thus be used as an indication of the progress of enolization through its three stages. The first stage is the same for glucose, mannose, and fructose and these should accordingly give a constant ratio, which is indeed borne out by the experiments. The third stage is the same for all the hexoses and it was found indeed that glucose and galactose, in strongly alkaline solutions, give the same ratio, indicating that the 3-4 enediol is principally oxidized. In weaker alkali these sugars give different ratios, presumably because of their different 1-2 and 2-3 enediols. The oxidation of *d*-mannitol, *d*-sorbitol and dulcitol by alkaline potassium permangate gives ratios which indicate that aldo-hexoses are the first oxidation-products and that *d*-sorbitol, which can conceivably pass either to *d*-glucose or *l*-gulose, follows the first course. An interesting example of a catalytic oxidation of carbohydrates in disodium phosphate solutions by air, the catalyst being a complex iron phosphate produced by dissolving ferrous sulfate in sodium pyrophosphate, was discovered by H. A. Spoehr [24] in 1924 and has now been further studied.[25] The

[22] Power and Upson, J. Am. Chem. Soc., **48**: 195; 1926.
[23] Jensen and Upson, J. Am. Chem. Soc., **47**: 3019; 1925.
[24] Spoehr, J. Am. Chem. Soc., **46**: 1494; 1924.
[25] Spoehr and Smith, J. Am. Chem. Soc., **48**: 236; 1926.

catalyst is not colloidal, gives none of the usual tests for iron, but it is readily oxidized by air and may exert its action by alternate oxidation and reduction. Its oxidation of carbohydrates yields carbon dioxide. Low concentrations of potassium cyanide accelerate the reaction but finely divided platinum and likewise insulin are without influence.

The physiological connection between the combustion of fats and glucose in the animal organism is an outstanding problem in metabolism. By experiments *in vitro* upon the oxidation of butyric acid and glucose by hydrogen peroxide in various alkaline media Witzemann [26] has studied the so-called β-oxidation of the acid, through which acetone is produced, and has demonstrated that an α-oxidation does also occur and therefore may possibly be a physiological process, but the presence of glucose does not influence the oxidation of the acid and the sugar thus exerts no anti-ketogenic influence like that observed during oxidation in the organism. An important contribution to this subject has been made by West [27] in showing that the oxidizability of acetoacetic ester is greatly increased by condensing it with various substances, and that it condenses with glucose to give a new type of sugar derivative which is oxidized with remarkable ease. This finding lends strong support to the theory developed by Geelmuyden,[28] Ringer,[29] Woodyatt,[30] and Shaffer [31] that "glucose is anti-ketogenic in human metabolism because it or one of its decomposition products combines with acetoacetic acid or other ketogenic molecule, forming a substance which is more easily oxidized in the organism than are the unchanged acetone bodies."

It is a fundamental question whether the metabolism of glucose may not involve a shifting of the dynamic equilibrium between the α- and β-forms of the sugar and other possible forms that its structure can conceivably take, such as the free aldehyde or the γ-glucose modifications. The search for experimental evidence of such changes has been vigorously prosecuted. The work of Clark [32] and of Winter and Smith [33] suggested that a change in the specific rotation of glucose can be detected for the glu-

[26] Witzemann, J. Am. Chem. Soc., **48**: 202, 208, 211; 1926.
[27] West, J. Biol. Chem., **66**: 63; 1925.
[28] Geelmuyden, Z. physiol. Chem., **41**: 136; 1904.
[29] Ringer, J. Biol. Chem., **17**: 107; 1914.
[30] Woodyatt, J. Am. Med. Assoc., **55**: 2109; 1910.
[31] Shaffer, J. Biol. Chem., **47**: 433, 449; 1921. **49**: 143; 1921. **54**: 399; 1922.
[32] Clark, J. Expl. Med., **26**: 721; 1917.
[33] Winter and Smith, J. Physiol., **57**: 100; 1923. Forest, Smith and Winter, J. Physiol., **57**: 224; 1923.

cose of the blood, which was interpreted as an indication of the preparation of glucose for utilization in the body, but further studies have caused other investigators [34] to dispute the existence of such experimental evidence. Lately the question has been revived through the announcement by Lundsgaard and Holbøll [35] that the action of insulin and muscle tissue upon glucose solutions *in vitro* causes a detectable change in rotatory power, which they interpret as due to the formation of a hypothetical substance provisionally named *new-glucose*. The accuracy of their experimental findings has been vigorously disputed by two investigators [36] who have repeated the experiments and obtained negative results. The change of rotation which Lundsgaard and Holbøll claim to have detected is so small that it borders on the limit of accuracy in polarimetric readings. Their claim of a maximum error of only 1.5% in reading a rotation of 0.3° Ventzke is doubtful to experienced polarimetric observers and the claim of 5% maximum error in reading a 0.1° rotation appears incredible. There is so far no trustworthy experimental evidence that the existence of new-glucose as a stage in the metabolism of the sugar has been demonstrated. The crystallization of insulin by Abel [37] stands out as an epoch-making discovery, the importance of which in the study of sugar metabolism cannot be overestimated.

The Action of Enzymes on Sugars.

A careful quantitative study of the influence of α-methyl glucoside in retarding the rate of hydrolysis of sucrose by invertase has been made by Nelson and Post.[38] References to the work by Paine and his collaborators from the Bureau of Chemistry, United States Dept. of Agriculture, on invertase and melibiase, have been mentioned in the first and second sections.

Studies Relating to the Structures of the Sugars.[38a]

The problem of the ring structures of the sugars and other carbohydrates is being studied so extensively today and such

[34] Hewitt, Brit. Med. J., I: 590; 1923. Eadie, Brit. Med. J., II: 60; 1923. Van Creveld, Biochem. J., 17: 556; 1923. Visscher, Am. J. Physiol., 68: 135; 1924. 76: 59; 1926. Denis and Hume, J. Biol. Chem., 60: 603; 1924.

[35] Lundsgaard and Holbøll, J. Biol. Chem., 62: 453; 1925. 65: 305, 323, 343, 363; 1925. 68: 457, 475, 485; 1926.

[36] Paul, J. Biol. Chem., 68: 426; 1926. Barbour, J. Biol. Chem., 67: 53; 1926.

[37] Abel, Proc. Nat. Acad. Sci., 12: 132; 1926.

[38] Nelson and Post, J. Biol. Chem., 68: 265; 1926.

[38a] An excellent review of recent researches from all countries on this subject has been published lately by J. Leibowitz, Z. angew. Chem., 39: 1143, 1240; 1926.

fundamental developments are being made in this field by many workers that it seems well to review the origin of the problem.

It is forty years ago that H. Kiliani [39] presented a remarkably clear program for the study of the structures of the sugars. Accepting the constitution of mannitol and dulcitol as $CH_2OH.(CHOH)_4.CH_2OH$, it was apparent that the hexoses glucose, fructose, and galactose could be regarded either as ketones or as aldehydes derived from such alcohols. Writing the aldehyde as $CH_2OH.(CHOH)_4.CHO$, it could be regarded as the anhydride of $CH_2OH.(CHOH)_4.CH(OH)_2$. On the other hand, this last structure could conceivably dehydrate by the loss of water from two hydroxyl groups, only one of which is attached to the aldehydic carbon atom and thus give a sugar having a ring structure of the type that Tollens had suggested in 1884, $CH_2OH.CHOH.CH.(CHOH)_2.CHOH$. Similar possibilities were apparent in the case of the ketone-alcohol structures. Kiliani then proposed the questions:

1. Is glucose (a) a ketone-alcohol or (b) an anhydride of the hypothetical hepta-atomic alcohol $CH_2OH.(CHOH)_4.CH(OH)_2$?

2. If it is (b), is its anhydro oxygen atom linked (c) to only one carbon atom, giving a true aldehyde, or (d) to two carbon atoms, giving a Tollens ring type of structure?

He added that "the assumption of such a ring formula will make the question of the structure of glucose very complicated because at least five such ring forms are conceivable." These precise formulations of Kiliani have lost none of their weight from later developments. Kiliani answered question one by proving that fructose has the structure of (a) and glucose that of (b). Fischer's application of the Van't Hoff-LeBel theory of the asymmetric carbon atom to the sugar structures and his proof of the configurations of the monosaccharides have not involved and therefore have not answered Kiliani's second question. However, a large mass of experimental data from the isolation of the α- and β-forms of many of the sugars and their derivatives, from the study of the mutarotation of the sugars and the action of enzymes on glucosides, and from the study of the methylated sugars and of rotatory relations in the sugar group have shown that the general case which Kiliani discussed is a true picture.

[39] Kiliani, Ber., 19: 768; 1886.

It is now generally accepted that all the structures which he formulated are capable of existence, and that probably most of them do exist in nature. The reality is indeed far more complicated in detail than Kiliani surmised, because the idea of the asymmetric carbon atom, which he had not included, greatly increases the number of structural possibilities. Thus for *d*-glucose there are apparently eleven possible isomeric forms, namely, an aldehyde form and an α- and β-form of each of five ring-type structures. It would be illogical to assume that any one of these forms is entirely lacking in a solution of glucose. The researches of the day are rapidly allocating precise structures to the monosaccharides and their derivatives, including the glycosides and compound sugars, but the unexplored field is so large that many years must still elapse before the structures of the principal carbohydrates of nature are known. Nevertheless, the problem has been formulated in precise terms and experimental methods of research have been devised which can hardly fail to disclose the facts sooner or later. The sugars offer today a most attractive field of research, the extent of which is remarkably large because the monosaccharides certainly react in most, if not all, of the ways that Kiliani discussed as the most general case, and experiment has shown that definite pure substances resulting from these various types of reaction can be isolated in the laboratory.

Much progress in the correlation of structures and rotatory powers in the sugar group has been made in America during the year. The rotation of chloroheptaacetyl lactose, which was somewhat exceptional in the theory, has been corrected through new measurements and the rotations of the corresponding bromo and iodo derivatives determined. The correct values agree with the theoretical predictions.[40] α-Methyl lyxoside, the rotation of which was exceptional, has been carefully purified and its true rotation found to have the predicted value.[41] The rotations of glucose, amylobiose and amylotriose appear to be related in a simple fashion, though the amorphous character of these compound sugars and their acetates necessarily leaves the experimental testing of the theoretical relations in some doubt.[42] The exceptional character of the rotations in the mannose and rhamnose series, which have attracted attention for many years past, now appear to be due to the occurrence of compounds of three

[40] Hudson and Kunz, J. Am. Chem. Soc., **47**: 2052; 1925.
[41] Phelps and Hudson, J. Am. Chem. Soc., **48**: 503; 1926.
[42] Hudson, Pringsheim and Leibowitz, J. Am. Chem. Soc., **48**: 288; 1926.

different ring types in these series. Mannose crystallizes in two forms, which have different ring structures, and is thus the first example of such behavior. A classification of the derivatives of mannose and rhamnose according to ring types has been made [43] and it is shown that when this grouping is applied to the glucose series [44] a proof that the α- and β-methyl glucosides and the α- and β-forms of glucose possess a 1,4 ring, results. This is at variance from the conclusions of Charlton, Haworth and Peat [45] and Levene and Simms,[46] who have given evidence from the velocity of lactone formation that these substances possess a 1,5 ring. Hirst [47] has also concluded from the oxidation of tetramethyl glucose to trimethoxy xylo-glutaric acid that the ring in the methyl glucosides is 1,5. Since the methods of study by which these disagreeing conclusions have been reached have little experimental material in common, it will require further experimental studies to bring the views into agreement. This question is one of the most important problems in the theoretical chemistry of the sugars today, and the obtaining of further evidence bearing upon it is much to be desired. Interesting halogeno-acetyl derivatives of salicin have been described by Kunz,[48] who has also performed the synthesis of salicin from *o*-cresyl *d*-glucoside. Parks and Anderson [49] have measured the heat capacities, entropies and free energies of mannitol and erythritol. Levene and Meyer [50] have begun a study of the relation of structure and optical rotation for the methylated acids of the sugar group and report data on the rotations of several methylated gluconic acids and their salts. Two articles by Levene and Sobotka [51] give an experimental verification of the recent very important work of Dale [52] by the repreparation of his crystalline α- and β-forms of tetraacetylmethyl *d*-mannoside. This verification is most welcome because the rotations of the α-, β-, and γ-forms which Dale discovered, taken in connection with those of the similar forms of triacetylmethyl *l*-rhamnoside of Fischer, Bergmann and Rabe,[53] have lately assumed fundamental significance

[43] Hudson, J. Am. Chem. Soc., **48**: 1424; 1926.
[44] Hudson, J. Am. Chem. Soc., **48**: 1434; 1926.
[45] J. Chem. Soc., **1926**: 89.
[46] J. Biol. Chem., **65**: 31; 1925. **68**: 737; 1926.
[47] Hirst, J. Chem. Soc., **1926**: 350.
[48] Kunz, J. Am. Chem. Soc., **48**: 262; 1926.
[49] Parks and Anderson, J. Am. Chem. Soc., **48**: 1507; 1926.
[50] Levene and Meyer, J. Biol. Chem., **65**: 535; 1925.
[51] Levene and Sobotka, J. Biol. Chem., **67**: 759, 771; 1926.
[52] Dale, J. Am. Chem. Soc., **46**: 1046; 1924.
[53] Fischer, Bergmann and Rabe, Ber., **53**: 2362; 1920.

in opening a way for the determination of the ring structures of the whole carbohydrate group (references 43 and 44). The crystalline γ-tetra-acetyl-ethyl *d*-mannoside ($[\alpha]_D = -27.6°$ in chloroform) which Levene and Sobotka have discovered is evidently the ethyl analog of Dale's γ-methyl derivative and doubtless possesses the latter's 1,C (= 1,3) ring structure. Levene and Sobotka offer the valuable suggestion that a provisional *cis-trans* classification of acetates of the sugar group having ring structures indicates that the trans form predominates in conditions of equilibrium and that it regularly shows a lower melting point than the corresponding cis form. Such a rule, if fully substantiated, would be very useful as an indication of structure. They also advance important evidence that the common forms of the halogeno-acetyl sugars have the same spatial configurations as the β-glucosides.

Chapter XXVII.

Fermentation Industries.

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Since the advent of prohibition in the United States the former scope of the fermentation industries in this country has been contracted due to the fact that America is no longer interested in the brewing industries proper,—the portion of the industry in which foreign interest and progress is still largely found. Another post-war development has, however, been largely instrumental in recent advances in this field. War needs brought out a new commercial source of acetone by a fermentation process with butanol (*n*-butyl alcohol) simultaneously produced. Efforts to find uses for large accumulated stocks of the latter material, together with other timely factors, were largely responsible for the development of the modern nitrocellulose lacquer industry which has grown at a phenomenal rate during the past few years. This development, in turn, has opened an extensive field for many other solvent materials.

The industries which depend fundamentally upon fermentation are few in number and are concerned chiefly, at present, in the production of ethanol, butanol, acetone, acetic acid (vinegar) and yeast, together with, in smaller measure, the production of lactic acid. The industries, while few in number, are responsible for the production of an imposing annual output. The latest figures available on ethanol output cover the year 1925 and indicate sales of approximately 85,000,000 wine gallons, of which 46,000,000 were sold as completely denatured, some 35,000,000 as specially denatured alcohol. The fermentation process which produces butanol and acetone showed an increased production of about 50% above that of the previous year. Probably more than 7,000,000 gallons of these two materials were manufactured.

Lactic acid totaled the equivalent of 2,500,000 lbs. of 100% acid.

The past twelve months period has seen a number of changes in the organization of the fermentation industry. A number of independent plants for the production of ethanol have been consolidated under the name of the American Solvents & Chemical Corporation,—a factor which should lead to better distribution of output and more efficient operation. One new plant, the first constructed since the conclusion of the World War, was built and put into operation by the Eastern Alcohol Co.

Early in 1926 the first book relating entirely to this field appeared. This book, "Industrial Fermentations" by Paul W. Allen,[1] while incomplete in a number of respects, contains in a compact form a great deal of information of value to the industry.

Among the developments in the methods of producing ethanol should be noted the following: Dahlberg [2] ferments a mash by yeast and beet extractive matter containing an organic nitrogen compound. Campbell [3] prepares fermentable worts by suspending the solid material from which the wort is to be prepared in a solvent liquid and then allowing it to settle in a plurality of layers. Part of the liquid is withdrawn and a portion of the withdrawn liquid is circulated through the layers to extract soluble substances from them. Deckebach [4] describes an apparatus for making beer of low alcohol content. A closed fermenting vat is provided with temperature-regulating coils and is connected to a condenser for recovery of vaporized alcohol. Rodebush [5] prepares highly concentrated alcohol by distilling 95% alcohol to which ethyl acetate has been added. According to Clapp [6] absolute alcohol may be obtained by distilling alcohol containing water with a hydrocarbon of low boiling point such as benzol in a column still. The hydrocarbon is used in quantity equivalent to 10½-17 times that of the water associated with the alcohol supplied to the still. Steffens [7] distils alcohol containing water in a column with an added third liquid such as benzol miscible with alcohol but substantially immiscible with water to obtain absolute alcohol at the bottom of the column.

Interest in yeast production, which is closely related to the

[1] Chemical Catalog Co., New York City.
[2] U. S. P. 1,581,001; Apr. 13, 1926.
[3] U. S. P. 1,581,918; Apr. 20, 1926.
[4] U. S. P. 1,551,979; Sept. 1, 1925.
[5] U. S. P. 1,583,314; May 4, 1926.
[6] U. S. P. 1,586,732; June 1, 1926.
[7] U. S. P. 1,586,717-18; June 1, 1926.

ethanol industry, is shown by the results obtained by a number of workers. Neil [8] describes a means for inhibiting the deterioration of compressed yeast by the incorporation of equal parts of yeast and a powder obtained by the evaporation of cows' milk, cooked arrowroot powder and a small amount of water. Pollak [9] describes a method for the production of a richly nitrogeneous food for yeast production. Sak [10] carries out a continuous process for the production of yeast which comprises the steps of preparing a yeast-nutrient mash, filtering the same, washing the residue, and initiating propagation of yeast with aëration in the wash water, and during the period of propagation substantially continuously adding the filtered wort and maintaining the temperature of the liquid within a range of 25-30° C. Wegener [11] prepares a compact body containing yeast imbedded in invert sugar, such sugar constituting at least 65% of said body, and the latter containing not more than 25% of water. Willstätter and Sobotka [12] prepare an article for use as a baking or brewing preparation consisting of yeast and at least one-third of its weight of maltose mixed therewith. Hoffman and Cregor [13] describe the manufacture of bakers' yeast which comprises a mash by gelatinizing starch-containing materials, saccharifying the mass with malt and digesting with papin, filtering off the liquid and thereafter propagating yeast therein with aëration. Corby and Glasgow [14] describe the preparation of a yeast nutrient solution consisting essentially of molasses, cereal material and yeast nourishing salts and in which an acidity is produced somewhat in excess of that preferable for yeast propagation. Kusserow [15] in preparing a yeast nutrient solution dilutes molasses containing lactic acid bacteria with water, adds an acid such as sulfuric to affect acidification without sterilization, and then a thiosulfate. Wroten [16] describes the preparation of a fermentable solution for the growth of yeast, containing "bone precipitate." Dahlberg [17] in making bakers' yeast uses a nutrient comprising as one ingredient the waste water resulting from the desugaring of beet molasses when the sugar is removed as an

[8] U. S. P. 1,557,764; Oct. 20, 1925.
[9] U. S. P. 1,558,627; Oct. 27, 1925.
[10] U. S. P. 1,566,431; Dec. 22, 1925.
[11] U. S. P. 1,570,418; Jan. 19, 1926.
[12] U. S. P. 1,574,776; Mar. 2, 1926.
[13] U. S. P. 1,575,761; Mar. 9, 1926.
[14] U. S. P. 1,571,932; Feb. 9, 1926.
[15] U. S. P. 1,580,500; Apr. 13, 1926.
[16] U. S. P. 1,580,550; Apr. 13, 1926.
[17] U. S. P. 1,580,999, 1,581,000; Apr. 13. 1926.

alkaline earth saccharate. Van Loon [18] finds that the activity of yeast or other ferment is enhanced by the addition of "per compounds" such as benzoylperoxide, acetylbenzoylperoxide, peracetic acid, the salts of organic peroxides, inorganic peroxides, etc. Richards [19] gives the results of a study on the effect of calcium sulfate on the growth and fermentation of yeast. Bauer [20] gives a review of the latest investigations in yeast and fermentation.

During the year greatly increased production of butanol and acetone took place due to increased plant capacity and operating economics. Several new processes and improvements on existing processes were perfected. Waters [21] claims a process which comprises adding to a sterilized mash of a carbohydrate material other than corn meal but containing corn protein, a culture of bacteria derivable from ordinary corn meal, sufficiently heat resistant to withstand a temperature of 80° C. for about twenty minutes and capable of producing in the presence of air butanol and acetone by fermentation of a sterilized corn meal solution and maintaining the thus treated carbohydrated mash at a temperature from about 32-36° C. until fermentation is about completed. Ricard [22] describes a process of fermenting carbohydrate materials to produce butanol and acetone which comprises forming a nonaseptic wort of amylaceous materials by boiling same to a concentration not to exceed 30% of the mass, then diluting the same and adding a relatively small quantity of such diluted wort to an aseptic fermenting carbohydrate wort to be fermented therewith. Strange [23] prepares alcohols and acetone in which both yeast and bacteria of the type of Fitz are added to a fermentable mash made from molasses and other fermentable material. Boinot [24] claims that the addition of lactates to a carbohydrate mash undergoing butanol-acetonic fermentation brings about an increase in the yield of butanol and a corresponding reduction in the proportion of acetone formed. This process, if successful, should mark a broad step forward, in that it tends to increase the production of the more valuable butanol at the expense of the cheaper acetone. Legg [25] describes a fermentation process which

[18] Eng. Pat. 248,373.
[19] J. Am. Chem. Soc., 47: 671; 1925.
[20] Am. Food J., 20: 351; 1925.
[21] U. S. P. 1,546,694; July 21, 1925.
[22] U. S. P. 1,550,746; Aug. 25, 1925. Can. Pat. 220,546.
[23] U. S. P. 1,550,928; Aug. 25, 1925. Eng. Pat. 251,678.
[24] U. S. P. 1,565,543; Dec. 15, 1925. Can. Pat. 253,511.
[25] U. S. P. 1,583,408; Apr. 27, 1926. Eng. Pat. 249,833. Can. Pat. 260,929.

consists in preparing a sterilized mash of protein-free carbohydrate and soluble nitrogenous matter derived from maize, inoculating the mash with butyl bacilli, allowing fermentation to proceed, and recovering butanol and acetone from the fermented mash. Broderick and Marvel [23] determined the composition of "yellow oil" obtained in the manufacture of butanol by fermentation.

Considerable attention has been devoted recently in other countries to the production of acetone by fermentation. Bakonyi [27] states that high yields of acetone and ethanol are obtained by the fermentation of starch and sugar by *Bacillus macerans* or *Bacillus acetoethylicus*. Cass [28] also discusses foreign developments in this field. Moskovitz [29] converts corn into acetone by the aid of *B. macerans* and a reducing agent similar to hydrosulfite, thiosulfate or sulfite; the latter compounds act unfavorably upon noxious organisms but do not prevent the acetone fermentation.

Search is being made continually for new sources of raw material. The work of Gokhale [30] upon mahua flowers as a raw material for the acetone fermentation process is worthy of note.

In connection with the butanol-acetone industry, no review of the year would be complete without reference to the patent infringement suit [31] by Commercial Solvents Corporation against Synthetic Products Co., Ltd., in the English Courts for alleged infringement of Weizmann's Eng. Pat. 4845 of 1915, in which the validity of the patent was upheld. This suit is worthy of note as being the first bacteriological case that ever appeared before the courts.

The search for new solvent materials and products which might be employed in internal combustion engines has recently led to the birth of another industry based on a fermentation process. Société LeFranc et Cie [32] has constructed a small plant near Paris for the production of ketol by the LeFranc process. The butyric acid fermentation is carried out in the presence of calcium carbonate, thus forming calcium butyrate which is dry-distilled. By the latter process dipropyl with a mixture of other ketones is obtained.

Although lactic acid is assuming greater importance as its uses increase it is still a minor industry and the developments

[26] J. Am. Chem. Soc., 47:3050; 1925.
[27] Biochem. Z., 169: 125-8; 1926. Chem. Ztg., Apr. 10, 1926; pp. 257-8.
[28] Industrial Chem., May, 1926; pp. 200-1.
[29] Aust. Pat. 100,444.
[30] J. Indian. Inst. Sci., 7, part 7: 84-7; 1925.
[31] Chemical Age (London), 14: 327; 1926.
[32] La Nature, March 27, 1926; p. 209. F. P. 541,535 and addition to F. P. 541,535.

during the past year have not been extensive. Faithful [33] recommends that during the production of lactic acid by fermentation of solution containing glucose or similar carbohydrate material, air or oxygen be injected to inhibit formation of butyric acid.

A number of other processes suggested during the past year, while not as yet of commercial importance, indicate the present trend of development in the fermentation industries. McDermott [34] prepares glycerol by inducing a vigorous fermentation by means of yeast in a molasses mash and then rendering the mash alkaline by successive small doses of sodium carbonate. Sinclair [35] describes a process for obtaining aldehydes from cacti which consists in mashing the same without adding water under conditions favorable to fermentation by its indigenous fungus, hydrolyzing the fully fermented pulp, and distilling the latter. Szucs [36] recommends that citric acid be prepared by fermentation, employing molasses as the culture medium and initiating fermentation by means of races of fungi of the genus *Citromyces, Mucor, Aspergillus,* and *Penicillium.* Langwell [37] describes conditions suitable for fermenting cellulose to form ethanol, acetic acid and butyric acid. Falck [38] prepares oxalic acid by subjecting mixtures of wood with calcium carbonate and cheap vegetable matter, to the action of wood-destroying fungi. Viljoen, Fred and Peterson [39] have isolated a thermophilic organism, similar to those used by Langwell, which converts cellulose to ethanol, acetic and butyric acids.

Opportunities for future developments in the fermentation industries lie in many directions. Organisms producing higher yields and more resistant to the many factors which influence their growth will do much for the industry. The utilization of vast quantities of by-product materials is almost an untouched field. At present some effort is being put forth to utilize the waste distillery slops in the form of cattle feed or as a fertilizer. Due to the fact that a portion of the unused material is in the form of suspended solids and a portion in solution it has been found difficult to fully recover it economically from the large amounts of water necessary to handle. Reich [40] proposes

[33] U. S. P. 1,569,221; Jan. 12, 1926. F. P. 607,995.
[34] U. S. P. 1,551,997; Sept. 1, 1925.
[35] U. S. P. 1,569,339; Jan. 12, 1926.
[36] Can. P. 251,180. Aust. P. 101,009.
[37] Eng. P. 248,795. Fr. P. 604,277.
[38] German P. 419.911.
[39] J. Agr. Sci., 16: 1-17; 1926.
[40] U. S. P. 1,552,732; Sept. 8, 1925.

to treat waste mixtures such as distilling slop, with ammonium sulfate in order to convert the potassium compounds to potassium sulfate and form a product adapted for use as a fertilizer.

One of the large problems yet to be solved on a commercial scale is the utilization of the gases liberated during fermentation. In the formation of ethanol, carbon dioxide is given off; the butanol-acetone fermentation gives [41] 62.61% of carbon dioxide and 1.60% of hydrogen based on the weight of carbohydrate used. In other words, one pound of fermented corn yields, in addition to other products, 5.5 cu. ft. of hydrogen. It is thus evident that this process gives a cheap source of hydrogen which can be obtained with little difficulty in a very pure form. Recent developments in the field of high pressure gas synthesis have opened up promising uses for hydrogen for the production of such compounds as ammonia, methanol, formaldehyde, formic acid, "synthol," etc. At present one company is constructing a plant for the production of synthetic ammonia, having a capacity of 15 tons per day, in order to utilize hydrogen produced by this method.

The utilization of the large amounts of carbon dioxide produced in both of the processes mentioned above would mark a step forward and serve to reduce present production costs appreciably. A development of the past year seems to indicate at least one promising solution to this problem. Several companies have begun the manufacture of "Dry Ice," which is a trade name for compressed carbon dioxide snow. It is claimed [42] that this product can be shipped to points within a radius of 500 miles of the plant, and that a chunk weighing half a pound or less will keep four times its bulk of liquid frozen solid for twenty-

Material	1913 Price	Peak Price	Price (July 1, 1926)
Denatured alcohol ...	35¢-38¢ gal.	$1.11 (1920)	29¢-32¢ gal.
Fusel oil (crude)	$1.35-1.50 gal.	$5.75 (1918)	$1.25-1.40 gal.
Butanol	.....	30¢-35¢ lb. (1921)	17½¢-20¢ lb.
Lactic acid (22% dark)	2½¢-4¢ lb.	6½¢-7½¢ lb. (1917)	5½¢-6¢ lb.
Acetone C.P.	13½¢-15½¢ lb.	35¢-36¢ lb. (1917)	11¢-13¢ lb.

[41] J. Soc. Chem. Ind., 45: 71; 1926.
[42] Drug Markets, 19: 155; 1926.

four hours. Such a material offers many advantages over ordinary ice.

Prices for products of fermentation have not advanced with other commodities and remain practically at pre-war levels.

The higher unit costs for raw materials, labor and fuel have been offset by increased production, efficiency and improvements in the processes of making fermentation chemicals.

The writer is indebted to Mr. Frank M. Crawford of the Research Information Department of the Commercial Solvents Corporation for his assistance in gathering most of the data presented in this review.

Chapter XXVIII.

Biochemistry.

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Acid-Base Metabolism. Fiske, Goodell, Hathaway, and West [1] determined a large loss of mineral base after a dose of sulfuric acid. Alma Hiller [2] found that injection of histamine into dogs, producing a state of shock resembling that following trauma, results in an internal acidosis, with a fall in blood p_H and CO_2, quite unaccompanied by the usual acid excretion in the urine. Peters, Bulger, Eisenman, and Lee [3] have made extensive studies of the acid-base balance in normal and diseased subjects under varying conditions. Palmer [4] has improved the Palmer-Van Slyke method for titration of organic acids in urine, and pointed out necessary precautions.

Amino Acid Physiology. Sherman and Woods [5] have determined the cystine content of proteins by the novel biological method of ascertaining the rate of growth of rats when fed on the protein plus an otherwise cystine-free diet. Dakin [6] has continued his studies on the mechanisms by which amino and fatty acids are broken down in the body. Cox and Rose [7] have found that histidine in the diet of rats can be replaced by synthetic *dl*-β-4-imidazole lactic acid; they have accordingly achieved the replacement of an indispensable amino acid by a non-amino compound. Morgulis [8] has brought added evidence that the liver is the organ in which amino acids are transformed into urea.

[1] Fiske, Goodell, Hathaway, and West, J. Biol. Chem., **67**: 385; 1926.
[2] Hiller, J. Biol. Chem., **68**: 833; 1926.
[3] Peters, Bulger, Eisenman, and Lee, J. Biol. Chem., **67**: 140-235; 1925.
[4] Palmer, J. Biol. Chem., **68**: 245; 1926.
[5] Sherman and Woods, J. Biol. Chem., **66**: 29; 1925.
[6] Dakin, J. Biol. Chem., **67**: 341; 1926.
[7] Cox and Rose, J. Biol. Chem., **68**: 769, 781; 1926.
[8] Morgulis, J. Biol. Chem., **66**: 353; 1925.

Amino Acid Chemistry. Hanke [9] has devised a colorimetric method for estimating tyrosine and histidine, and has determined them in a number of proteins. Pratt [10] has improved the method of preparing arginine.

Basal Metabolism. Blunt, Tilt, McLaughlin, and Gunn [11] have accumulated data to serve as standards for girls between 8 and 18 years.

Blood Physical Chemistry. Murray and Hastings [12] have formulated graphically the equilibria in blood among the variables H_2CO_3, HCO_3', CO_3', Ca, and PO_4, and the physiological effects thereon of respiration and renal excretion. Murray and Henderson [13] have estimated the "diffusing capacity of the capillary bed." Murray and Morgan [14] have estimated and graphically represented the interplay of the effects of oxygen consumption, blood flow, hemoglobin content, and oxygen diffusing capacity. Hastings and Sendroy [15] have determined by precise experiments the effects of variations in ionic strength of salt solutions on the apparent first and second dissociation constants of carbonic acid. Van Slyke, Hastings, Murray, and Sendroy [16] have estimated the ratios of Cl, HCO_3, and active H^+ ions between cells and serum, have correlated them with Donnan's law, and have estimated the ratio of the activity coefficients of Cl' and HCO_3' in cells to those in serum. Atchley and Nichols [17] have determined the effect of protein concentration on the conductivity of serum. Stadie, Austin, and Robinson [18] have ascertained the effect of temperature on the CO_2 absorption curves of blood and serum, and on the acid-base-protein equilibrium represented by these curves. Pincus, Peterson, and Kramer [19] have determined the proportions of serum calcium and phosphate that are filterable through collodion in normal and diseased sera. McClendon [20] has devised apparatus for use of the direct current in determining the electrical conductivity of blood. Cullen and Bülmann [21] have worked out conditions for determination of blood p_H with the

[9] Hanke, J. Biol. Chem., **66**: 475; 1925.
[10] Pratt, J. Biol. Chem., **67**: 351; 1926.
[11] Blunt, Tilt, McLaughlin, and Gunn, J. Biol. Chem., **67**: 491; 1926.
[12] Murray and Hastings J. Biol. Chem., **65**: 265; 1925.
[13] Murray and Henderson, J. Biol. Chem., **65**: 407; 1925.
[14] Murray and Morgan, J. Biol. Chem., **65**: 419; 1925.
[15] Hastings and Sendroy, J. Biol. Chem., **65**: 445; 1925.
[16] Van Slyke, Hastings, Murray, and Sendroy, J. Biol. Chem., **65**: 701; 1925.
[17] Atchley and Nichols, J. Biol. Chem., **65**: 729; 1925.
[18] Stadie, Austin, and Robinson, J. Biol. Chem., **66**: 901; 1925.
[19] Pincus, Peterson, and Kramer, J. Biol. Chem., **68**: 601; 1926.
[20] McClendon, J. Biol. Chem., **68**: 653; 1926.
[21] Cullen and Bülmann, J. Biol. Chem., **64**: 727; 1925.

quinhydrone electrode. Austin, Stadie, and Robinson [22] have studied the relations between the colorimetrically apparent p_H of serum or plasma, observed with phenol red indicator, and the standard p_H determined electrometrically. Fricke [23] has studied the electrical resistance and capacity of blood.

Physiology of Calcium and of Calcification. Holt, La Mer, and Chown [24] have studied the solubility products of $Ca_3(PO_4)_2$ in serum, and have come to the conclusion that serum is supersaturated with this salt, even in rickets when Ca or PO_4 or both are abnormally low. Holt [25] also finds the spinal fluid supersaturated. Hammett [26] has studied the changes in the mineral composition of the bones during growth.

Collip and Clark [27] have continued their studies on the parathyroid hormone and the results of its effect in raising the blood calcium content, and have advanced the purification of the hormone.[28] Hjort, Robison, and Tendick [29] have confirmed Collip and added further observations. Greenwald and Gross [30] have found that administration of parathyroid hormone causes a negative calcium balance. The increase of Ca in circulation therefore comes from dissolved bone, and not from increased absorption of food calcium.

Hjort,[31] Greenwald,[32] and Irving [33] have shown that soluble calcium salts given by mouth in large amounts may be absorbed rapidly enough to raise the blood calcium content and relieve tetany, caused by calcium deficit.

Denis and Corley [34] have studied the calcium content in tissues.

Blood Sugar. Hiller, Linder, and Van Slyke [35] find that 10% to 30% of the blood sugar determined by the current reduction methods cannot be glucose, as it is not fermentable by yeast. Similarly Harned [36] by treating blood filtrate with mercuric nitrate and $NaHCO_3$, and thereby removing the nitrogenous substances, diminished the sugar content, determined by the Folin-Wu method

[22] Austin, Stadie, and Robinson, J. Biol. Chem., **66**: 505; 1925.
[23] Fricke, J. Gen. Physiol., **9**: 137, 153; 1925.
[24] Holt, La Mer, and Chown, J. Biol. Chem., **64**: 509, 567, 579; 1925.
[25] Holt, J. Biol. Chem., **66**: 23; 1925.
[26] Hammett, J. Biol. Chem., **64**: 685, 693; 1925.
[27] Collip and Clark, J. Biol. Chem., **64**: 485; 1925.
[28] Collip and Clark, J. Biol. Chem., **66**: 133; 1925.
[29] Hjort, Robison, and Tendick, J. Biol. Chem., **65**: 117; 1925.
[30] Greenwald and Gross, J. Biol. Chem., **68**: 325; 1926.
[31] Hjort, J. Biol. Chem., **65**: 783; 1925.
[32] Greenwald, J. Biol. Chem., **67**: 1; 1925.
[33] Irving, J. Biol. Chem., **68**: 513; 1926.
[34] Denis and Corley, J. Biol. Chem., **66**: 609; 1925.
[35] Hiller, Linder, and Van Slyke, J. Biol. Chem., **64**: 625; 1925.
[36] Harned, J. Biol. Chem., **65**: 555; 1925.

by 17% to 25%. These results favor the accuracy of Benedict's recent blood sugar method, which yields figures averaging about 20% lower than those previously in use.

Carbohydrate Metabolism. Voegtlin, Thompson, and Dunn [37] show that glycerol feeding may triple the blood sugar content; hence glycerol is converted into glucose. Cori and Cori [38] find by blood analysis that chicken tumor turns glucose to lactic acid faster than does the normal tissue, confirming Warburg's observation on isolated pieces of tissues. The same authors [39] demonstrate beautifully by determining the gas exchange and the final total glycogen content of rats that administration of insulin to rats accelerates both combustion of administered glucose and its transformation into glycogen, about half the glucose being used for each. Richardson, Levine, and Du Bois [40] show by total metabolism determinations that patients with exophthalmic goitre store glycogen normally. By similar determinations Wierzuchowski [41] finds that in phorhizin diabetes of dogs some sugar can be burned.

Enzymes. Nelson and Post [42] have studied further the mode of action of invertase. Noyes, Lorberblatt, and Falk [43] have studied, on a series of esters and at varying temperatures from 5° to 55°, the ester-hydrolyzing reaction of extracts from a number of animal and vegetable sources. In some cases the higher temperature caused so rapid destruction of enzyme that the rate of hydrolysis was less than at lower. Hussey and Thompson [44] have studied the rate of inactivation of invertase and pepsin by the radiations from radium emanation, and find that the logarithmic decrease in enzyme is proportional to the radiant energy. In further studies [45] they show that the effect of the gamma radiation is negligible compared to that of the beta, and that inactivation speed is but slightly affected by temperature. Northrop [46] shows that the immunity of the substance of living organisms to attack by pepsin and trypsin is due to failure of the enzymes to penetrate the living cells.

[37] Voegtlin, Thompson, and Dunn, J. Biol. Chem., **64**: 639; 1925.
[38] Cori and Cori, J. Biol. Chem., **65**: 397; 1925.
[39] Cori and Cori, J. Biol. Chem., **67**:xlvii; 1926.
[40] Richardson, Levine, and Du Bois, J. Biol. Chem., **67**: 737; 1926.
[41] Wierzuchowski, J. Biol. Chem., **68**: 385; 1926.
[42] Nelson and Post, J. Biol. Chem., **68**: 265; 1926.
[43] Noyes, Lorberblatt, and Falk, J. Biol. Chem., **68**: 135; 1926.
[44] Hussey and Thompson, J. Gen. Physiol., **9**: 211, 217; 1925.
[45] Hussey and Thompson, J. Gen. Physiol., **9**: 309, 315; 1925.
[46] Northrop, J. Gen. Physiol., **9**: 497; 1926.

Mineral Metabolism. Miller [47] finds that feeding large amounts of potassium causes only initial transitory losses of other bases, insufficient to alter the mineral composition of the body. Sherman and Quinn [48] present a careful study of the phosphorus content of rats' bodies during growth.

Chemistry of Renal Physiology. Wearn and Richards,[49] by a series of extraordinary micro-analyses, have studied the chloride content of the urine from single glomeruli of the frog's kidney, and found that it was greater than that of the urine in the bladder, showing that reabsorption of more chloride than water occurred in the tubules.

Phosphatides. Levene and Rolf [50] have studied the lecithin, cephalin, and cuorin of the soy bean, isolating the fatty acids and glycero-phosphoric acid of the lecithin. The same authors [51] isolated different bromolecithins from liver and egg yolk, indicating the presence of several different lecithins in each.

Sulfur Compounds. Benedict, Newton, and Behre [52] have isolated from pig and human blood a substance of elementary composition $C_{12}H_{20}N_4O_3S$, which contains no amino nitrogen, and like uric acid, generates a blue color with the Folin uric-acid reagent.

Vitamines. In the difficult task of purifying the vitamines Levene and Van der Hoeven [53] have progressed by combined physical and chemical methods to highly potent preparations of vitamine B from yeast, such that 0.02 mg. is active in curing polyneuritis in birds. The accumulation and storage of vitamine A in the animal body has been quantitatively followed by Sherman and Cammack.[54] Mattill and Clayton [55] have added evidence to the existence of a vitamine E necessary for reproduction.

[47] Miller, J. Biol. Chem., **67**: 71; 1925.
[48] Sherman and Quinn, J. Biol. Chem., **67**: 667; 1926.
[49] Wearn and Richards, J. Biol. Chem., **66**: 247; 1925.
[50] Levene and Rolf, J. Biol. Chem., **68**: 285; 1926.
[51] Levene and Rolf, J. Biol. Chem., **67**: 659; 1926.
[52] Benedict, Newton, and Behre, J. Biol. Chem., **67**: 267; 1925.
[53] Levene and Van der Hoeven, J. Biol. Chem., **65**: 483; 1925.
[54] Sherman and Cammack, J. Biol. Chem., **68**: 69; 1926.
[55] Mattill and Clayton, J. Biol. Chem., **68**: 665; 1926.

Chapter XXIX.

Photochemistry.*

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Research in photochemistry in the United States is localised in a comparatively few centres. Indeed, of some twenty-five publications in this field during the period under review all save two or three have come from the laboratories in Cambridge, Madison, Berkeley, Pasadena and Princeton. There is need for an expansion of interest in the subject since, as is evident from a very excellent review of progress, published in the Annual Reports of the London Chemical Society, by Professor A. J. Allmand, covering the years 1914-1925 there are problems and to spare for the curious-minded. And, in that the assistance of the physicist, with his new ideas on activation and excitation of atoms and molecules, as revealed by spectroscopic studies, is increasingly available, the great problem of chemical activation should receive renewed study by the photochemist.

For progress in photochemical technique one turns naturally to the laboratory of G. S. Forbes [1] at Harvard who this year has provided the experimentalist with valuable new data of the energy distribution in the spectra of mercury vapor arcs under a variety of working conditions. Especially useful for workers with restricted resources are the constricted mercury arcs which are described. Also from Harvard comes investigation of a chlorine gas filler for the 2536 Å line of the mercury arc and a comparison of it with the chlorine-bromine filter as permitting the use of a reasonably monochromatic light source.[2] A filter of this type is

* Comprising in part the report of the Committee on Photochemistry for the year 1925-1926. Hugh S. Taylor, Chairman; Wilder D. Bancroft, Farrington Daniels, G. S. Forbes, Samuel C. Lind, and Herman A. Spoehr.

[1] Harrison and Forbes, J. Am. Chem. Soc., **47**: 2449; 1925.

[2] Villars, J. Am. Chem. Soc., **48**: 1874; 1926.

now marketed by the Hanovia Chemical and Manufacturing Company and has given good service in the Princeton laboratory.

The nature of unimolecular thermal reactions was the object of two researches which appeared simultaneously in which the decomposition of nitrogen pentoxide under the influence of infra red radiation was studied by H. A. Taylor [3] in New York University and F. Daniels [4] in Wisconsin. Both authors agree that infra red radiation introduced photochemically into nitrogen pentoxide is without measurable effect. The problem therefore still remains as to what causes unimolecular reactions, collisions, radiations or what. From the Madison Laboratories also comes a study by Mason and Mathews [5] of the acceleration of the oxidation of sodium sulfite by ultra-violet light and the influence of accelerants and inhibitors on the process. Their work shows that there are still many problems in this important field, since there is no general unifying principle underlying the observations. Another photosensitive oxidation that has received study is that of a variety of leuco bases.[6] Such work has varied interest, as the basis of a possible photo-process and as related to the problems of fluorescence and chemiluminescence.

Two excellent studies of photo-decomposition are recorded by Porter [7] and his students in the University of California. They deal with the vapors of acetone and formic acid. In both cases the absorption spectra were determined. The study with acetone was of interest as contributing to the stock of information in answer to the query "Is one quantum photochemically as good as another?" Porter and Iddings find that, within the absorption band, the outer wave lengths are as efficient as the head of the band, when corrected for differences in extent of absorption. The formic acid case was of interest in that ultra-violet light causes decomposition to both water and carbon monoxide and hydrogen and carbon dioxide, as do various contact catalysts.

No year of work in photochemistry would be complete without some phase of the century-old photochemical union of hydrogen and chlorine receiving attention. This year there are three important papers from Princeton University by Marshall.[8] In the

[3] J. Am. Chem. Soc., **48**: 577; 1926.
[4] J. Am. Chem. Soc., **48**: 607; 1926.
[5] J. Phys. Chem., **30**: 414; 1926.
[6] Carroll, J. Phys. Chem., **30**: 130; 1926.
[7] Porter and Iddings, J. Am. Chem. Soc., **48**: 40; 1926. Ramsperger and Porter, *ibidem*, **48**: 1267; 1926.
[8] J. Phys. Chem., **29**: 842, 1453; 1925. **30**: 757; 1926.

first he brings to experimental test the production of hydrogen chloride by introduction of hydrogen atoms, prepared by Wood's method, into unilluminated hydrogen and chlorine. Using bromine, in separate experiments, as a measure of hydrogen atoms introduced, he concludes that more hydrogen chloride is produced than corresponds to hydrogen atoms employed. This points to some type of chain mechanism, possibly that of Nernst—

$$\begin{aligned} Cl_2 + \text{light} &= 2Cl \\ Cl + H_2 &= HCl + H \\ H + Cl_2 &= HCl + Cl. \end{aligned}$$

In the second communication he demonstrates that, at low partial pressures of the two gases, the photochemical yield per quantum of light absorbed is very small as compared with the yield at atmospheric pressures. From 0.001 mm. to 6 cm. the quantum yield changes from 6 to 250,000 molecules per quantum—the chains are less efficient at low pressures. In the third communication he repeats, with considerable experimental improvement, the old experiments of Bodenstein and Taylor, who illuminated chlorine and led it into unilluminated hydrogen. Marshall reduced the interval between illumination and mixing from 0.0006 sec. to 0.0001 sec., using purer gases than did Bodenstein and Taylor. As with them, however, his results were negative. More work is needed to account for this and Marshall suggests some such work.

A great deal of attention has been given during this year to processes photosensitised by mercury. Dickinson showed in 1924 that hydrogen and oxygen at low pressures, in the presence of mercury vapor, would react at room temperatures when illuminated with the resonance radiation ($\lambda = 2537$ Å) from a cooled mercury arc. Taylor and Marshall [9] greatly simplified the technique by operation at atmospheric pressure. They showed that oxygen, ethylene, carbon monoxide and nitrous oxide could all be rapidly reduced in this way. The mechanism involved is the collision between an excited mercury atom and a hydrogen molecule whereby, presumably, hydrogen atoms result. These are the active agents in the reduction. Further investigation [10] has shown that hydrogen peroxide is the first isolable product in the reaction with oxygen and that it can be obtained thus as 100% H_2O_2.

[9] J. Phys. Chem., 29: 1140; 1925.
[10] Taylor, Marshall, Bates, Nature, 117: 267; 1926. Marshall, J. Phys. Chem., 30: 34; 1926.

Formaldehyde is the major product from carbon monoxide. Olsen and Meyers [11] showed that, at low pressures, in presence of ethylene, the rate was proportional to the square root of the hydrogen pressure, thus probably involving atoms of hydrogen. They showed also that, under the influence of mercury, polymerisation of ethylene occurs. Bates and Taylor [12] have shown that this involves elimination of hydrogen from ethylene, formation of some acetylene and a volatile mercury organic compound. Rideal and Hirst [13] suspected that a liquid mercury surface was the active catalytic agent, but it has been decisively proved that this is not necessary. More work is needed to elucidate what actually happens when an excited mercury atom and a hydrogen molecule collide. Is the product two hydrogen atoms and a normal mercury atom or is it mercury hydride and one hydrogen atom? Some recent work by Dickinson and Sherrill [14] shows that excited mercury and pure oxygen yield ozone. From the energy relationships involved, they suggest that the collision produces an excited oxygen molecule which then reacts with a normal molecule to form ozone.

Whether the formation of an excited molecule or dissociation into atoms is involved in the activation of hydrogen bromide and hydrogen iodide prior to their photo-decomposition has been approached by Tingey and Gerke.[15] They call to their assistance the newer work of the physicists on the absorption spectra of molecules. From their experimental conclusion that the absorption spectra of these molecules are continuous and not banded they conclude that absorption of light results in dissociation, not in an excited molecule. This conclusion supports Warburg's mechanism for the photodecomposition.

$$\begin{aligned} HX + \text{Light} &= H + X \\ H + HX &= H_2 + X \\ X + X &= X_2 \end{aligned}$$

as opposed to Stern and Volmer's

$$\begin{aligned} HX + \text{Light} &= HX' \text{ (excited)} \\ HX' + HX &= H_2 + X_2. \end{aligned}$$

We need independent methods of test of these hypotheses.

[11] J. Am. Chem. Soc., **48**: 389; 1926.
[12] Taylor, Proc. Am. Phil. Soc., **65**: 90; 1926.
[13] Nature, **116**: 899; 1925. Proc. Camb. Phil. Soc., **23**: 162; 1926.
[14] Proc. Nat. Acad. Sci., **12**: 178; 1926.
[15] J. Am. Chem. Soc., **48**: 1838; 1926.

Chapter XXX.

Colloid Chemistry.*

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This survey deals primarily with the more important contributions of American chemists to the general theory of colloid science during the past year. Contact catalysis, which is a colloid chemical phenomenon, is considered in another section as are the applications of colloid science to industry, agriculture, geology, biology, and medicine.

Colloidal Solutions

Distinction between true and colloidal solutions. In a great many cases the distinction between true and colloidal solutions can be made by applying the criterion of Gibbs. According to Gibbs, an apparent phase is not a one-phase system unless the properties are definitely defined when the temperature, pressure, and concentration are fixed. By applying this test, it may be shown readily that most colloidal solutions are two-phase systems. The difficulty comes with solutions of such substances as tannin and soaps which appear to satisfy Gibbs' criterion for a one-phase system when in reality they are two-phase systems. A similar situation is encountered with a mixture of two gases which, in the last analysis, is neither physically nor chemically homogeneous but which is a one-phase system nevertheless. To take care of these cases, W. D. Bancroft[1] assumes that any gas or vapor will pass through any pore through which any other gas or vapor will pass. If this unproved but reasonable assumption is granted, it leads directly to the conclusion that any substance which can

* Comprising in part the report of the Committee on the Chemistry of Colloids for the year 1925-1926. Harry B. Weiser, Chairman; Wilder D. Bancroft, Floyd E. Bartell, Eugene C. Bingham, Ross A. Gortner, Harry N. Holmes, J. Howard Mathews, S. E. Sheppard, E. B. Spear, and J. A. Wilson.

[1] Colloid Symposium Monograph, 3: 17; 1925. J. Phys. Chem., 29: 966; 1925.

be filtered out by an ultrafilter is in colloidal solution and not in true solution, an ultrafilter being defined as a porous membrane which shows no marked negative adsorption, that is, specific adsorption of the solvent. This criterion puts soap and tannin in the list of colloidal solutions and would undoubtedly take care of the highly dispersed solutions of such substances as molybdenum trioxide and molybdenum blue. It should be pointed out, however, that any apparent solution which will pass through the finest ultrafilter is not *necessarily* in true solution.

Stability. Applying the phase rule to colloids, Rice [2] deduces that both when particles are electrically charged and when they are not, equilibrium exists only when the particles are all of one size or of a few definite sizes. Two distinct types of stability are recognized, temporary and permanent. The conditions for stability and the relations for the two kinds of stability are discussed and the considerations applied to coagulation.

The addition of electrolytes to a sol which owes its charge to preferential adsorption of ions, causes coagulation when the charge on the particles is reduced below a critical value by adsorption of ions of the electrolyte having a charge opposite to that on the sol. Since adsorption of the ions having the same charge as the sol, the stabilizing ions, cannot be disregarded, particularly with electrolytes that precipitate only in high concentrations, the precipitation value of an electrolyte for a sol is that concentration which results in sufficient adsorption of the precipitating ion to neutralize the combined adsorption of the original stabilizing ion and the stabilizing ion added with the electrolyte.[3] In so far as influences other than the adsorbability of the precipitating ion may be disregarded, one should expect the precipitating power of an electrolyte to be greater, the greater the adsorbability of the precipitating ion. Furthermore, one should expect an ion of high valence to be adsorbed more strongly than an ion of low valence to the extent that the precipitating power of an electrolyte increases with increasing valence of the precipitating ion in accord with Schulze's Law. The accuracy of these conclusions has been verified experimentally by Weiser.[4] N. R. Dhar [5] and his collaborators believe, however, that the ion which precipitates in highest concentration is adsorbed the most—a view that appears

[2] J. Phys. Chem., **30**: 189; 1926.
[3] Weiser, J. Phys. Chem., **28**: 232; 1924.
[4] J. Phys. Chem., **29**: 955; 1925.
[5] Dhar, Sen, and Ghosh, J. Phys. Chem., **28**: 457; 1924.

to be unsound both theoretically and experimentally. Weiser [6] studied the precipitation of sols by salt pairs and showed that the precipitation values may be additive, may be greater than the additive values, or may be less than the additive values. The determining factors are (1) the effect of each precipitating ion on the adsorption of the other (ionic antagonism), (2) the stabilizing action of ions having the same charge as the sol, and (3) the relatively greater adsorbability of ions at lower concentrations.

C. Gurchot [7] investigated the reversibility of coagulation of copper ferrocyanide sols and of membranes of copper ferrocyanide supported by gelatin jelly. The membranes like the sols are granular, the space between the granules being filled with adsorbed water. The membranes are coagulated more or less completely by low concentrations of methyl alcohol, acetic acid, sodium chloride, potassium chloride, and calcium chloride thereby becoming permeable to sugar. The coagulation and hence the permeability of the membranes is reversible. It is suggested that the intermittent permeability in living membranes is probably also a question of reversible coagulation. L. V. Heilbrunn [8] cites evidence to support the view that the surface membrane of cells is charged negatively while the interior of the cell is filled with positively charged particles. The fluidity of the interior protoplasm is increased by cations in the order $Al''' , Ce''' > Ca'' , Mg'' > Na$.

A stable negative sol of barium sulfate is formed in the presence of sodium citrate. M. L. Nichols and O. J. Thies, Jr.,[9] have determined the conditions favorably for sol formation and have shown that determinations involving the precipitation of barium sulfate can be made satisfactorily by adding slightly more than enough acid to convert the citrate to citric acid before precipitation is begun. H. V. Tartar and C. F. Draves [10] call attention to the importance of hydrogen ion concentration for the stability of mastic sols. All sols of one variety of mastic precipitate at about the same pH with hydrochloric acid alone, regardless of the concentration or dispersity. In the pH range beyond 6 they all precipitate with nearly the same concentration of potassium chloride.

[6] J. Phys. Chem., 30: 20; 1926.
[7] J. Phys. Chem., 30: 83; 1926.
[8] Colloid Symposium Monograph, 3: 135; 1925.
[9] J. Am. Chem. Soc., 48: 302; 1926.
[10] J. Phys. Chem., 30: 763; 1926.

J. N. Kuglemass [11] made an extended physico-chemical study of the mechanism of blood clotting. A clot is formed only between $p_H = 4.75$ and $p_H = 8$, these limits defining the isoelectric points of sero-globulin ($p_H = 4.55$) and sero-albumin ($p_H = 4.7$) on the one side and that of fibronogen ($p_H = 8$) on the other side. Ionic antagonism between sodium and calcium, which is always present, affects the clotting time and syneresis. Excess calcium retards clotting to a greater extent than sodium. Excess calcium retards syneresis while excess sodium favors the process. J. Oliver and P. Smith [12] studied the kinetics of the agglomeration of red blood cells suspended in 8.5% glucose solution. Although the particles are approximately 50,000 times larger than colloidal gold particles and have a much slower Brownian movement, the blood cells form aggregates as rapidly as colloidal gold particles. L. S. Palmer and G. A. Richardson [13] showed conclusively that colloidal protection is not involved in the coagulation of cow's milk by the addition of a small amount of rennin. Although the exact mechanism of the process is not understood, the colloidal rennin enzyme apparently changes the nature of colloidal calcium caseinate in such a way that it is readily coagulated by cations.

J. B. Nichols and H. C. Liebe [14] discuss the theory of the centrifugal method for the determination of the distribution of size of particles of suspended material. Measurements of the distribution of size of particles for six representative lithopones were measured and compared with the respective obscuring powers of the pigments. C. A. Mann [15] considers the mechanism of lithopone formation to consist in the mutual precipitation of positively charged barium sulfate and negatively charged zinc sulfide.

In an interesting and suggestive paper H. T. Barnes [16] has described his observations on colloidal water and ice.

Surface Tension. On allowing a 0.1 M solution of sodium nonylate to stand it appears cloudy and has the very low surface tension of 0.2 dyne per square centimeter.[17] On making the solute 0.005 molar with respect to NaOH the surface tension becomes 45.4 and at 0.008 M, 48.8. The extremely low surface tension is probably due to a surface film of sodium nonylate and nonylic acid resulting from hydrolysis. Sodium hydroxide re-

[11] Colloid Symposium Monograph, 3: 158; 1925.
[12] J. Phys. Chem., 30: 1; 1926.
[13] Colloid Symposium Monograph, 3: 112; 1925.
[14] Colloid Symposium Monograph, 3: 268; 1925.
[15] Colloid Symposium Monograph, 3: 247; 1925.
[16] Colloid Symposium Monograph, 3: 99; 1926.
[17] Harkins and Clark, J. Am. Chem. Soc., 47: 1854; 1925.

presses the hydrolysis and raises the surface tension due to removal of the acid. P. L. du Nüoy [18] emphasizes the difference between static and dynamic surface tension of colloidal solutions. Surface tension measurements on egg albumen with a special tensimeter [19] at dilutions between 1/700,000 and 1/250,000 revealed the existence of numerous minima. From the two principal minima occurring most frequently, the dimensions of the "phantom shape" of the molecule are calculated to be 41.7×10^{-8} cm. and 30.8×10^{-8} cm. Assuming the "phantom shape" to be a parallelopiped, the upper limit of the molecular weight is calculated to be 30,800.[20]

Emulsions

Observations by W. Seifriz [21] on the effect of acidity on the behavior of olive oil emulsions, preclude ascribing to acidity the prime rôle in determining type or reversibility of emulsions. Alteration of the phase-volume ratio has no effect on the type of emulsion of petroleum oils of light weight stabilized by casein; but such oils in or near the zone of instability are readily influenced by change in ratio of the oil and water phases. The observations cannot be accounted for on the basis of our present theories of emulsification and it is probable that some factor has been overlooked. The behavior of certain vegetable oils as regards emulsification is compared with petroleum oils. W. Rieman and P. A. van der Meulen [22] studied emulsions of oil in water containing a solution of phenol in toluene as the internal phase and sodium oleate as emulsifying agent. Variation in the soap concentration in the external phase and of phenol in the internal phase causes a variation in the average area of interface covered per molecule of soap. Within the range studied the protective film is composed of a monomolecular layer of oriented molecules. In a general paper on the distribution and orientation of molecules, I. Langmuir [23] discusses the orientation of molecules at an interface. W. D. Harkins and H. Zollman [24] determined the interfacial tension between phases of water and benzene in the presence of sodium oleate alone or with addition of sodium hydroxide, sodium chloride, or oleic acid. If the aqueous phase is 0.1 N with respect

[18] Colloid Symposium Monograph, 3: 25; 1925.
[19] du Nüoy, Biochem. Z., 155: 113; 1925. *Cf. also* J. Gen. Physiol., 7: 625; 1925. Compt. rend., 180: 1570; 1925.
[20] du Nüoy, J. Biol. Chem., 64: 595; 1925.
[21] J. Phys. Chem., 29: 834; 1925.
[22] J. Am. Chem. Soc., 47: 2507; 1925.
[23] Colloid Symposium Monograph, 3: 48; 1925. *Cf. also* Harkins and McLaughlin, J. Am. Chem. Soc., 47: 1610; 1925.
[24] J. Am. Chem. Soc., 48: 69; 1926.

to both NaCl and NaOH, the tension has the remarkably low value of 0.04 dyne per cm. Similar results obtain with 0.001 N sodium oleate. Calcium chloride largely overcomes the effect of sodium chloride even though the former is 50 times more dilute. With an interfacial tension below 10 dynes per cm. the benzene emulsifies easily in the aqueous phase; and when below 1 dyne it emulsifies spontaneously.

A. J. Stamm [25] investigated the dispersity of emulsions by determining the distribution of the size of the particles. Method of preparation is the prime factor in determining the dispersity. Different monovalent soaps give the same mass maxima. An excess of alkali increases the dispersity of oil-in-water type of emulsions but decreases the dispersity of the reverse type for the smaller dispersed particles. The oriented wedge theory of emulsification is inadequate to explain the observations.

R. M. Cobb [26] studied the effect of aging of soap solutions on their emulsifying and lathering power and R. M. Chapin [27] investigated the detergent action of soap. The evidence indicates that the colloidal fraction of a soap is inert as a detergent.

Gels

A critical investigation of the structure of gelatin jellies by E. O. Kraemer [28] leads him to conclude that jelly formation is the result of an incomplete or unsuccessful attempt at precipitation of a solid phase from a liquid system. A sol immediately precedes the jelly state.[29] The optical properties and general behavior of the jellies indicate a rather fine-grained structure; but the high vapor pressure of the water over a weak gelatin jelly and the very slight increase in resistance which such a jelly offers to the diffusion of ions and molecules, demonstrates that on a molecular scale, such gels do not possess the high rigidity which they display in bulk. The Brownian movement of mercury particles 200-250 μμ in radius were recorded with the kinoultramicroscope. The results indicate that the structure of weak gelatin jellies is finer than the indicating mercury particles. G. W. Scarth [30] concludes that gelatin jellies have a definite heterogeneous structure modifiable by swelling agents as well as by heat. Variations in the degree of swelling with change of p_H are attributed to changes in a

[25] Colloid Symposium Monograph, 3: 251; 1925.
[26] Ind. Eng. Chem., 17: 1134; 1925.
[27] Ind. Eng. Chem., 17: 1187; 1925.
[28] J. Phys. Chem., 29: 1523; 1925.
[29] *Cf. also* Weiser, Colloid Symposium Monograph, 1: 38; 1923.
[30] J. Phys. Chem., 29: 1009; 1925.

positive force attracting water rather than to contrary variations in bulk elasticity. It is believed that the elasticity and viscosity changes attending protoplasmic contraction are analogous to those attending the shrinkage of protein gels when acidified to the isoelectric point from a neutral or alkaline condition. B. L. Clark [31] investigated the general form of the curve relating swelling capacity of agar-agar to the water content immediately before swelling. The curve exhibits a well-defined maximum. An optical change occasioned by drying has been shown to be connected with the water-content-swelling relation. W. C. Arsem [32] considers a normal gel to consist of an associated phase and a free phase. The associated phase is regarded as an attenuated or expanded solid in which the molecular units are held together by residual valences but looser and more irregular than in a crystal. The free phase permeates the voids in the associated phase. Segregation of the associated phase into a fibrillar structure may take place and if shrinking occurs simultaneously, such aggregates as curds and clots may form. Changes in the rigidity of the solid phase are attributed to changes in the properties of free residual valences.

W. Siefriz [33] studied the elasticity of the sols and jellies of certain soaps. Sodium stearate elastic both as "sol" and jelly, has rod-shaped particles. From the solution of this soap, curd masses crystallize out. An inelastic sodium stearate possesses spherical particles and does not give a curd. Ammonium oleate forms a highly elastic dilute solution. A concentrated solution of this soap may be formed which is inelastic as a sol and highly elastic as a jelly.

G. L. Baker [34] investigated the effect of various factors on the strength of pectin jellies and M. A. Griggs and R. Johnstin [35] studied the preparation and properties of alcohol pectin jellies and sugar-acid pectin jellies. S. Klosky and C. Margano [36] prepared jellies of titania and mixed titania and ferric oxide jellies.

J. H. Yoe [37] finds that hydrous aluminum oxide precipitated at temperatures from 0 to 100° is always gelatinous. A granular mass is not formed at 66° as reported by W. E. Taylor.[38] L. B.

[31] J. Am. Chem. Soc., **47**: 1954; 1925. *Cf. also* Harvey, Am. J. Pharm., **97**: 447; 1925.
[32] J. Phys. Chem., **30**: 306; 1926.
[33] Colloid Symposium Monograph, **3**: 285; 1925.
[34] Ind. Eng. Chem., **18**: 89; 1926.
[35] Ind. Eng. Chem., **18**: 623; 1926.
[36] J. Phys. Chem., **29**: 1125; 1925.
[37] J. Phys. Chem., **29**: 1419; 1925.
[38] Chem. News, **103**: 169; 1911.

Miller [39] gives a comprehensive account of the effect of anions on the physical, colloidal, and chemical properties of hydrous aluminum oxide and emphasizes the importance of a careful control of conditions in order to obtain the best alumnia floc for water purification.

As a result of recent investigations on colloidal soil material carried out in the U. S. Bureau of Soils, P. L. Gile [40] believes the soil to consist chiefly of gels of silica, alumina, and iron oxide, together with organic matter and water. There is a fairly constant relation between the content silica, alumina, and iron oxide in different soil colloids and their properties. E. Truog [41] discusses the function of colloids in the soil and gives evidence to support the theory that soil acidity is due to complex acids. F. J. Alway [42] discusses the factors determining the power of soils to adsorb water from the air. F. O. Anderegg and R. P. Lietz [43] show how the colloidal content of the soil complicates the estimation of soil acidity by the thiocyanate method.

Proteins.

W. F. Hoffman and R. A. Gortner [44] have continued their extended physicochemical studies of the proteins [45] by comparing the behavior of H_3PO_4 with casein and durumin on titrating electrometrically with both NaOH and $Ca(OH)_2$ and back titrating with HCl. The alkali titration curves of casein and fibrin show binding of alkali at about $p_H = 5.5$ and resemble the curve for a weak acid such as NaH_2PO_4. Durumin behaves as a much weaker acid, beginning to bind alkali at about $p_H = 10$. Curves of the same type are obtained when a protein is titrated with either NaOH or $Ca(OH)_2$ but the curves are not similar when H_3PO_4 is titrated with NaOH and $Ca(OH)_2$.

A detailed investigation of the optical activity of gelatin systems lead E. O. Kraemer and J. R. Fanselow [46] to conclude that the evidence is insufficient to justify the statement of others [47] that gelatin contains two related molecular species.

The protective action of gelatin on gold sol was found by H.

[39] Colloid Symposium Monograph, 3: 208; 1925.
[40] Colloid Symposium Monograph, 3: 216; 1925.
[41] J. Am. Soc. Agron., 17: 280; 1925.
[42] Colloid Symposium Monograph, 3: 228; 1925.
[43] Ind. Eng. Chem., 17: 1153; 1925.
[44] J. Phys. Chem., 29: 769; 1925.
[45] Colloid Symposium Monograph, 2: 209-368; 1924.
[46] J. Phys. Chem., 29: 1169; 1925.
[47] *Cf.* Thomas and Kelly, J. Am. Chem. Soc., 47: 833; 1925.

V. Tartar and J. R. Lorah [48] to be influenced by the hydrogen ion concentration. Between p_H values 8 to 5 the hydrogen ion concentration has practically no influence on the protective action, but below $p_H = 4.7$ the protective action decreases very rapidly with increasing concentration of hydrogen ion. W. G. France [49] made a motion picture study of the influence of gelatin on the rates of crystal growth and solution of copper sulfate. Small concentrations of gelatin affect the rate of growth to a greater extent than they affect the rate of solution.

A. W. Thomas,[50] J. A. Wilson,[51] and K. H. Gustavson [52] have made numerous observations on the taking up of various tanning agents by collagen. All of these investigators consider the tanning of leather to be a chemical process in which definite chemical compounds are formed between the tanning substance and the collagen of the hide.

Adsorption.

J. S. Beekley and H. S. Taylor [53] studied the adsorption of univalent silver salts by silver iodide which has a definite crystal lattice even in the spongy precipitate employed. The order of adsorption is benzoate > acetate > nitrite > bromate > napthalenesulfonate > benzenesulfonate > nitrate > chlorate > ethyl sulfate > perchlorate. While this is not exactly the reverse of the order of solubilities of the salts, the less soluble ones are strongly adsorbed and the more soluble ones weakly adsorbed.

Using alumina as an adsorbent for water vapor L. A. Munro and F. M. G. Johnson [54] showed that the equations of both H. Freundlich and W. A. Patrick [55] apply to the isotherms at 60° and 80°. Neither applies to the isotherm obtained when the partial pressure approaches the vapor pressures of the liquid at the temperature of the adsorbent. Using silica gel as adsorbent, W. A. Patrick and C. E. Greider [56] determined the heat of adsorption of sulfur dioxide and water vapor at 0°. In both cases the difference

[48] J. Phys. Chem., **29**: 792; 1925.
[49] Colloid Symposium Monograph, **3**: 317; 1925.
[50] Thomas and Foster, J. Am. Chem. Soc., **48**: 489; 1926. Ind. Eng. Chem., **17**: 1167; 1925. Thomas and Kelly, J. Am. Chem. Soc., **48**: 1312; 1926. Ind. Eng. Chem., **18**: 136, 625; 1926. Thomas, *ibid.*, **18**: 259; 1926.
[51] Wilson and Bear, Ind. Eng. Chem., **18**: 84; 1926.
[52] Ind. Eng. Chem., **17**: 823; 1925.
[53] J. Phys. Chem., **29**: 942; 1925.
[54] J. Phys. Chem., **30**: 172; 1926. *Cf. also* Perry, *ibid.*, **29**: 1462; 1925.
[55] J. Am. Chem. Soc., **38**: 588; 1916. Patrick and Jones, J. Phys. Chem., **29**: 1; 1925. Patrick and Ebermann, *ibid.*, **29**: 220; 1925. Patrick and Lind, *ibid.*, **29**: 336; 1925. Patrick, Preston, and Owens, *ibid.*, **29**: 421; 1925. Patrick and Opdyke, *ibid.*, **29**: 601; 1925.
[56] J. Phys. Chem., **29**: 1031; 1925.

between the heat of adsorption and the heat of liquefaction is explained on the basis of surface energy considerations. The heat of adsorption of hydrogen on simple and promoted nickel catalysts was determined by C. F. Fryling.[57] The heat of adsorption-volume adsorbed curve for promoted catalysts possesses a maximum that is attributed to the formation of atomic hydrogen.

W. A. Patrick and E. H. Barclay [58] distinguished three types of adsorption; chemical, molecular layer, and capillary. The retention of alkali by silica gel is attributed to chemical forces and is given as an example of chemical adsorption in contradistinction to the taking up of gases and vapors by silica gel which is regarded as capillary condensation. H. N. Holmes, R. W. Sullivan, and N. W. Metcalf [59] give directions for markedly increasing the adsorbing capacity of silica gel by a moist heat treatment.

Data on the adsorption of gases by graphite carbon obtained by H. H. Lowry and S. O. Morgan [60] are in general agreement with the view that any treatment which will increase the ratio of surface to mass or the degree of unsaturation of the atomic forces of a solid adsorbent, or both, will increase its adsorption capacity. R. N. Traxler and F. E. E. Germann [61] showed that the decolorization of carbon bisulfide solutions of iodine with red phosphorus is not due to adsorption but to reaction with the phosphorus triiodide. The adsorption of ethylene and hydrogen by seven different catalysts was measured by W. A. Lazier and H. Adkins.[62] W. A. Patrick and P. W. Bachman showed that when mercury droplets are allowed to pass through dilute aqueous solutions of mercurous sulfate or acetate, the mercurous ions are adsorbed appreciably more than the sulfate or acetate. J. A. Wilkinson and W. Hoff [63] found the adsorption of dyes by soils to be of the same general nature as the dyeing of fibers. H. R. Thies [64] investigated the relation between dye adsorption in clays and the behavior of the latter in rubber. A clay that is good for rubber usage adsorbs but a small amount of dye.

Plasticity.

A Plasticity Symposium arranged by Professor Eugene C. Bingham was held at Lafayette College in October, 1924, and the

[57] J. Phys. Chem., **30**: 818; 1926.
[58] J. Phys. Chem., **29**: 1400; 1925.
[59] Ind. Eng. Chem., **18**: 386; 1926.
[60] J. Phys. Chem., **29**: 1105; 1925.
[61] J. Phys. Chem., **29**: 1119; 1925.
[62] J. Phys. Chem., **30**: 353; 1926.
[63] J. Phys. Chem., **29**: 808; 1925.
[64] Ind. Eng. Chem., **17**: 1165; 1925.

proceedings were published in the Journal of Physical Chemistry in October, 1925. The introduction to the Symposium was given by Bingham,[65] who defined plasticity and the related properties of substances. H. N. Holmes[66] pointed out that emulsifying agents are believed to form oriented monomolecular films at interfaces and that the viscosity of emulsions is affected by the nature of the emulsion film as well as by the volume concentration of the two phases. According to W. P. Davey,[67] the plasticity of single crystals has to do with the slipping of atoms upon adjacent planes, and so the relative plasticities of two crystals may be predicted from their crystal structure. W. D. Bancroft and L. E. Jenks[68] made a nonplastic kaolin very plastic by the addition of 0.25% lithium chloride. There is, however, no relation between the plasticity of a clay and its lithium content. It is probable that humus will have to be taken into account. From plasticity data of S. E. Sheppard[69] and melting point, specific rotation, and plasticity measurements of R. H. Bogue,[70] it is concluded that the transition temperature from gelatin jelly to sol is not definite but depends on the concentration and the method of preparation. C. S. Venable discussed the plasticity of viscose silk and pointed out the importance of the plasticity constant of viscose silk from both a technical and scientific standpoint. S. E. Sheppard and E. K. Carver[71] measured the plasticities of cuprammonium cellulose solutions and of nitrocotton in methyl alcohol. Considering the elastic behavior of cellulose esters under both steady and alternating stresses, they noted that these molecules behaved more like metals than like rubber. It is believed that the "solutions" consist of fibrils made up of chains of molecules held together by residual valences. C. Bergquist[72] recommends plasticity measurements on starch pastes for control purposes; and W. S. Crowell and A. Saunders[73] report the results of plasticity measurements on dental impression compounds.

W. H. Herschel and R. Bulkley[74] explain how the Ostwald viscosimeter may be used as a consistometer. E. Moness and

[65] J. Phys. Chem., 29: 1201; 1925.
[66] J. Phys. Chem., 29: 1205; 1925.
[67] J. Phys. Chem., 29: 1211; 1925.
[68] J. Phys. Chem., 29: 1215; 1925.
[69] J. Phys. Chem., 29: 1225; 1925.
[70] J. Phys. Chem., 29: 1233; 1925.
[71] J. Phys. Chem., 29: 1244; 1925.
[72] J. Phys. Chem., 29: 1264; 1925.
[73] J. Phys. Chem., 29: 1267; 1925.
[74] J. Phys. Chem., 29: 1217; 1925.

P. M. Giesey [75] describe a simple plastometer for control use with dental creams. H. Green and G. S. Haslam [76] have designed a microplastometer for studying plastic flow, and for determining the viscosity of liquids and the yield values of paints. P. K. Porter and W. A. Gruse [77] use a plastometer for measuring cup grease consistency.

Color.

C. W. Mason [78] has begun an investigation into the color of insects. In his first paper he reports that all whites of insects are structural colors. The pearly and metallic luster are due to superposed transparent parallel laminæ. Blue pigments do not appear to be present in insects but Tyndall blue occurs in a few insects. Structural conditions are found to modify the appearance of pigment colors very markedly. W. D. Bancroft [79] finds the color of certain blue woods to be a Tyndall blue and of certain blue roots to be a pigment color due to vivianite, a somewhat oxidized ferrous phosphate.

T. E. Phipps and W. R. Brodie [80] tested Stassfurt blue and sodium-colored halite for alkalinity. The former gave no alkalinity, which throws doubt on the theory that the Stassfurt blue color is due to colloidal sodium. It is suggested that Stassfurt blue may be an electronic color.

L. M. Currie [81] in Bancroft's laboratory finds the color of amorphous antimony sulfides to be yellow in a very fine state of subdivision and crimson when the amorphous particles are larger. The crystalline sulfide is black. Maroon shades are mixtures of crimson and black sulfides.

Problems.

A list of 200 research problems in colloid chemistry by W. D. Bancroft was published in Industrial and Engineering Chemistry and reprinted in 1921 as one of the Reprint and Circular Series of the National Research Council. This circular is now out of print. A few additional suggestions follow.

1. **Precipitation of Sols by Alcohol.** Many sols may be agglomerated wholly or in part by alcohol. A survey of the avail-

[75] J. Phys. Chem., **29**: 1289; 1925.
[76] Ind. Eng. Chem., **17**: 726; 1925.
[77] Ind. Eng. Chem., **17**: 953; 1925.
[78] J. Phys. Chem., **30**: 383; 1926.
[79] J. Phys. Chem., **30**: 521; 1926.
[80] J. Phys. Chem., **30**: 507; 1926.
[81] J. Phys. Chem., **30**: 205; 1926.

able data discloses that alcohol is much more effective in precipitating negative sols than positive ones. This phenomenon should be investigated systematically and an explanation formulated.

2. **The Effect of β and γ Rays from Radium on Ceric Oxide Sols.** Under the influence of a brief exposure to β and γ rays from radium a ceric oxide sol shows a rapid increase in viscosity to a maximum followed by a sharp drop. Fernau and Pauli [82] attribute this to the peptizing action of electrically charged particles entangled in the jelly. This view seems inadequate. Since hydrogen ion is the stabilizing ion of the sol, observations of the change in the hydrogen ion concentration might throw some light on the anomalous behavior during the aging process [83]

3. **Mutual Precipitation of Sols.** Biltz [84] investigated systematically the mutual precipitation of positively and negatively charged sols and on the basis of his data it is usually assumed that, although the optimum amount of a positive sol required to precipitate negative sols varies, the order is always the same.[85] As a matter of fact the order is not always the same,[86] which leads Bancroft to conclude that the phenomenon is specific, depending on the nature of the two colloids. Wintgen and Löwenthal [87] claim the mutual precipitation of oppositely charged sols to be a maximum when equal numbers of charges of opposite sign are mixed. If this be the case the phenomenon should not be influenced by the nature of the sol. Biltz's experiments should be repeated, under carefully controlled experimental conditions with well purified sols of known composition.

4. **Stability of Alumina Sol Prepared by Mechanical Disintegration.** Utzino [88] ground alumina in a colloid mill with glucose and claimed to get a sol the maximum stability of which does not occur with the finest state of subdivision. Some factor has been overlooked apparently, and the experiments should be repeated.

5. **Stability of Colloidal Lead Peroxide.** Colloidal PbO_2 is formed by hydrolysis of alkali metaplumbate. The behavior of this sol toward electrolytes appears anomalous in many respects.[89]

[82] Kolloid-Z., **20**: 20; 1917
[83] *Cf.* Weiser: The Hydrous Oxides, p. 256-8.
[84] Ber., **37**: 1095; 1904.
[85] Freundlich: Kapillarchemie, p. 445; 1909. Thomas in Bogue's Colloidal Behavior, **1**: 325; 1924.
[86] Bancroft: Applied Colloid Chemistry, p. 307; 1926.
[87] Z. physik. Chem., **109**: 391; 1924.
[88] Kolloid-Z., **32**: 149; 1923.
[89] Bellucci and Parravano, Atti. accad. Lincei, **15**, II: 542, 631; 1906.

A systematic study of the preparation and properties of the sol should be made.

6. **The Nature of Molybdenum Blue Solutions.** Dumanski reduced pure MoO_3 suspended in water with metallic molybdenum, obtaining an electrolyte-free solution which appeared optically empty until a small amount of electrolyte was added. Dumanski concludes that very pure molybdenum blue dissolves in water giving a true solution but that the presence of traces of electrolyte polymerizes the molecules. Since the blue as usually prepared contains adsorbed impurities, its solutions are colloidal. The observations of Dumanski should be confirmed, for, if the facts are as stated, they raise the question of the mechanism of the agglomeration of monomolecular molecules by the presence of traces of a variety of electrolytes. It is probable that Dumanski's pure blue solution is a sol.[90]

7. **The von Schröder Paradox.** von Schröder [91] studied the behavior of gelatin in liquid water and in water vapor and was led to conclude that the vapor pressure of water in gelatin must be higher than that of pure water because water distills from the gelatin to the vapor phase. Wolff and Büchner [92] claim that the alleged loss of water when gelatin is placed in the vapor phase is due to experimental error. While von Schröder's experiments are subject to criticism the errors pointed out by Wolff and Büchner seem insufficient to render the former's results worthless. Von Schröder's experiments should be repeated with the aid of McBain's adsorption balance [93] which would make it possible to carry out all observations in a closed system.

8. **The Stability of Blue Cupric Oxide.** Weiser [94] showed that the stability of blue cupric oxide at 100° in the presence of certain salts was due to a change in physical character from a gelatinous to a dense modification that does not darken readily. Since only those salts are effective in low concentration which give an acid reaction by hydrolysis the transformation was attributed to the solvent action of the solutions. Fowles [95] rules out this alleged solvent action and assumes that the heavy metal salts remove alkali, a catalyst, which hastens the darkening. This hypothesis is not particularly helpful or constructive since it does

[90] *Cf.* Weiser, The Hydrous Oxides, p. 284-8.
[91] Z. physik. Chem., **45**: 109; 1903.
[92] Z. physik. Chem., **89**: 271; 1915.
[93] McBain and Baker, J. Am. Chem. Soc., **48**: 690; 1926.
[94] J. Phys. Chem., **25**: 501; 1923.
[95] Chem. News, **128**: 5; 1924.

not attempt to define the nature of the alleged catalytic action on the dehydration process.

Quartaroli [96] claims that one part of hydrogen peroxide in 200 million of water accelerates the darkening of blue hydrous cupric oxide suspended in dilute alkali. The mechanism of this process proposed by Quartaroli is so vague and indefinite that the observations should be confirmed and extended.

9. **The Color of Cobalt Oxides.** Cobalt oxide is either rose-colored or blue, depending on the conditions of formation. Hantzsch [97] believes that the two forms are hydrate isomers, but this seems unlikely since apparently one may have either a blue or rose oxide in the absence of water. Weiser [98] suggests that the difference in color is due to a difference in the size of the particles. An alternative hypothesis is that there are two allotropic forms of cobalt oxide, an unstable blue one and a stable rose. The existence or non-existence of allotropic forms could probably be settled by comparing X-radiograms of the blue and rose oxides or hydrates.

Benedict observed that nickel salt retards the rate of transformation of the blue hydrous oxide to rose. This action of nickel salt is specific. It is suggested [99] but not proven, that the specific action may be due to nickel oxide having the same crystal lattice as cobalt oxide.

10. **The Simultaneous Adsorption of Two Precipitating Ions in the Neutralization of Sols.** From a study of the mutual adsorption of sulfate and oxalate during the precipitation of alumina, Miller [100] concludes that the taking up of ions is a solid solution phenomenon. This seems improbable and the observations should be repeated and extended to different adsorbents and to ions which show marked differences in adsorbability.[101]

11. **Non-aqueous Colloidal Solutions.** A systematic investigation should be made of sols and gels with liquids other than water, giving special attention to methods of formation and the factors influencing stability.

12. **Peptization by Mixed Solvents.** Many cases are known where mixed solvents peptize a solid much better than either one alone. A notable example is the peptization of cellulose nitrates with mixtures of ether and alcohol. A satisfactory theory of this

[96] Gazz. chim. ital., **55**: 264; 1925.
[97] Z. anorg. Chem., **73**: 304; 1911.
[98] The Hydrous Oxides, p. 147-150.
[99] The Hydrous Oxides, p. 148.
[100] U. S. Public Health Repts., **39**: 1502; 1924.
[101] *Cf.* Weiser, The Hydrous Oxides, p. 127-8.

action has not been worked out; but Bancroft [102] suggests that one of the liquids may occur in two forms in equilibrium with each other and that the second liquid displaces this equilibrium in such a way as to produce a concentration of the active modification sufficiently great to cause peptization.

[102] Applied Colloid Chemistry, p. 200; 1926.

Chapter XXXI.

Catalysis.*

By Hugh S. Taylor,

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The student aspiring to an intensive training in the subject of catalysis is fortunate if situated in the United States. During the last decade, progress in the development of the many aspects of this subject has nowhere been more encouraging than in this country. In numerous centres, various special branches of the subject are studied under the supervision of recognised authorities. At Cornell under Bancroft, at Virginia under Pease and Benton, and at Princeton, phases of the theoretical problems involved in contact catalysis are under study. Catalysis in organic chemistry is the motif of much work by Reid at Johns Hopkins, Adams at Illinois, Adkins at Wisconsin and Gomberg at Michigan. Homogeneous catalysis and its bearing on the newer theories of solution are under study by Bray at California and Harned of Pennsylvania. Special problems have their centres, as, for example, catalytic oxidation of carbon monoxide by Frazer of Hopkins, Lamb of Harvard, Bray of California; X-rays and catalysis at Washington with Wyckoff and at Cambridge under Clark; nitrogen fixation at the Fixed Nitrogen Research Laboratory, Washington, and in several industrial laboratories. In spite of all this educational work chemists trained in catalysis are still very scarce, are constantly being sought by the industries dependent on the catalyst, nitrogen fixation, hydrogenation, contact sulfuric acid, the organic chemical industry, the petroleum, paint and varnish industries and, not least, the new methanol industry.

The present status of the theoretical problem in contact catalysis has recently been comprehensively stated in the Fourth Report of

* Comprising in part the report of the Committee on Contact Catalysis for the year 1925-1926. Wilder D. Bancroft, Chairman, Homer Adkins, E. Frankland Armstrong, William C. Bray, O. W. Brown, R. F. Chambers, Colin G. Fink, J. C. W. Frazer, E. Emmet Reid, and Hugh S. Taylor.

the Committee on Contact Catalysis.[1] Much of the newer work is amplifying the point of view therein expressed. Thus, Pease and Cook,[2] in their study of the nickel steam equilibrium, conclusively show that a portion of the nickel surface has abnormally large activity, the same being true of the nickel oxide in the reverse reduction. The importance of the nickel-nickel oxide interface is re-emphasized in the studies of Benton and Emmett [3] of the catalytic synthesis of water vapor. The study of promoted catalysts is progressing. An excellent X-ray study by Wyckoff and Crittenden [4] of promoted iron catalysts showed that the promoter decreased the size of the iron crystals and so extended the available surface. Russell and Taylor [5] showed that extension of surface alone was not sufficient to account for all the promoter effect, but that the promoter also increased the fraction of active surface atoms. Poisoning studies on iron catalysts (by Almquist, not yet published) confirm this. Kunsman [6] has shown that iron promoted catalysts have excellent properties as positive ion emitters, though these properties have not yet been associated with the catalytic activity. Clark [7] attempted to correlate X-ray studies of nickel catalysts with their catalytic activities. The results are less convincing than those of Wyckoff and Crittenden already discussed. Sputtered films of platinum and nickel have, according to Gauger,[8] no catalytic activity.

Pease and Stewart [9] have added calcium to the list of metals that catalyse the combination of hydrogen and ethylene. Adkins and Lazier [10] studied the adsorptions of hydrogen and ethylene on various catalysts. The significance of adsorption studies has already passed far beyond the stage when such measurements have much value, a criticism also true of a recent paper from the Badische Laboratory by Schmidt. As pointed out by Pease and by the writer in the Fourth Report, it is the low pressure adsorption that is important. Why this is so in hydrogenation studies is evident from the work of Wolfenden [11] in Princeton who showed that hydrogen adsorbed at low pressures is probably

[1] Taylor, J. Phys. Chem., **30**: 145; 1926.
[2] J. Am. Chem. Soc., **48**: 1199; 1926.
[3] J. Am. Chem. Soc., **48**: 632; 1926.
[4] J. Am. Chem. Soc., **47**: 2866; 1925.
[5] J. Phys. Chem., **29**: 1325; 1925.
[6] J. Phys. Chem., **30**: 525; 1926.
[7] J. Am. Chem. Soc., **47**: 2661; 1925.
[8] J. Am. Chem. Soc., **48**: 2278; 1926.
[9] J. Am. Chem. Soc., **47**: 2763; 1925.
[10] J. Phys. Chem., **30**: 353; 1926.
[11] Proc. Roy. Soc., 110A: 464; 1926.

atomic. The parallel researches on the properties of atomic hydrogen are discussed in the section on photochemistry. The addition of chlorine to ethylene is, like the addition of bromine, a surface reaction occurring on the walls of the containing vessel.[12]

There are several communications during the period in question dealing with oxide catalysts. The preparation of ether from alcohol in contact with alumina was studied by R. H. Clark, Graham and Winter.[13] The views of Bosworth and Dilworth [14] on alumina as catalyst are somewhat heterodox. Engelder and his coworkers [15] have returned to the study of dehydration with titania and other catalysts. Adkins and Lazier [16] have restated their views as to the action of oxide catalysts in combined dehydrogenation-dehydration processes. As is well known, Adkins believes that the spacing of active centres in the catalyst is of importance, whereas Taylor believes that many results attributed to spacing may be caused by poisons. The two points of view are set forth in the Fourth Report. More work is yet needed since some newer views of Taylor [17] indicate that oxide catalysts are in reality *dual* catalysts, in which the metal ions and the oxide ions exercise different functions, the former a dehydrogenating action, the latter a dehydrating action.

Among oxide catalysts of oxidation, the mixture of oxides of copper and manganese, Hopcalite, has been further studied by Hoskins and Bray.[18] The chief technical use of oxide catalysts is in the drying of oils and several papers dealing with this subject have appeared. Ludwig [19] discusses the use of lead and manganese as driers. Rhodes and Cooper [20] compare the yellow and brown oxides of iron as agents for oxidation of oil. Zinc oxide receives a separate study by Rhodes and Mathes.[21] Ochres tend first to retard and then to accelerate the drying of the oil. The initial retardation is ascribed to adsorption of the drier from the oil, the final acceleration to the formation of iron soaps which act as catalysts. Zinc oxide is not an oxidation catalyst but may cause coagulation in the oil medium.

Inhibitors are equally as important as catalysts, both theoreti-

[12] Stewart and Fowler, J. Am. Chem. Soc., **48**: 1187; 1926.
[13] J. Am. Chem. Soc., **47**: 2748; 1925.
[14] J. Phys. Chem., **29**: 1489; 1925.
[15] J. Phys. Chem., **30**: 106, 476; 1926.
[16] J. Am. Chem. Soc., **48**: 1671; 1926.
[17] 4th National Symposium on Colloid Chemistry, Cambridge, June, 1926.
[18] J. Am. Chem. Soc., **48**: 1454; 1926.
[19] Ind. Eng. Chem., **17**: 1160; 1925.
[20] Ind. Eng. Chem., **17**: 1255; 1925.
[21] Ind. Eng. Chem., **18**: 30; 1926.

cally and practically. Smith and Wood [22] have supplied some quantitative evidence of the effect of inhibitors on the oxidation of unsaturated oils. Another important phase of this problem is the mechanism of the action of anti-knock materials. The most important contribution on this subject thus far is that of Church, Mack and Boord,[23] who see in such substances as lead tetraethyl materials decomposing to yield a fine metallic dust of catalytic activity, causing rapid oxidation uniformly throughout the gas mixture instead of a wave travelling with increasing velocity until a detonation wave sets up (knock). The work of Clark, Brugmann and Thee [24] suggests that the earlier view that ionization was suppressed by anti-knock materials is probably incorrect.

In homogeneous catalysis the main effort at present is directed towards bringing the data of reaction velocity in solutions into harmony with the results of thermodynamic treatment of solutions. The data of Livingston and Bray and of Livingston [25] on the decomposition of hydrogen peroxide solutions in acid-halide mixtures constitute an important step in establishing such a relationship. Brönsted and King [26] have made a study of salt effect on hydroxyl ion catalysis and have thereby further tested Brönsted's activity theory of the salt effect. Some data by Taylor and Close [27] on acid catalysis in lactone formation in several solvents should be examined in the light of the activity theory of catalysis. Yost [28] has studied the catalytic activity of silver ions as oxidation catalysts.

In the realm of catalytic organic synthesis, perhaps the most interesting achievement is the reduction of cinnamic aldehyde to cinnamyl alcohol in the presence of a treated platinum catalyst. Tuley and Adams [29] have shown that selective reduction of the aldehyde grouping can be secured with the production of almost pure cinnamyl alcohol. The platinum catalyst must be employed in the presence of small amounts of both zinc and iron salts. No more than one molecular equivalent of hydrogen is adsorbed in striking contrast to the behaviour with other catalysts with which phenylpropyl alcohol is normally produced. There is no real explanation, as yet, for the protective action of the zinc on the

[22] Ind. Eng. Chem., **18**: 691; 1926.
[23] Ind. Eng. Chem., **18**: 334; 1926.
[24] Ind. Eng. Chem., **17**: 1226; 1925.
[25] J. Am. Chem. Soc., **47**: 2069; 1925. **48**: 53; 1926.
[26] J. Am. Chem. Soc., **47**: 2523; 1925.
[27] J. Phys. Chem., **29**: 1085; 1925.
[28] J. Am. Chem. Soc., **48**: 374; 1926.
[29] J. Am. Chem. Soc., **47**: 3061; 1925.

double bond in the side chain of the aldehyde. Carothers and Jones [30] have shown that the Adams platinum catalyst permits the smooth reduction of nitriles to primary amines without production of secondary amines. The catalytic reduction of nitronaphthalene has been studied by Parrett and Lowy,[31] in glycol, water and isopropyl alcohol as solvents using palladium and platinum as catalyst. The efficiency of the media increased in the order given. Increased pressure favored the reduction. High percentage yields were obtained in 1.5 hours in the temperature range 70-100° C. Molten α-nitronaphthalene was reduced efficiently in presence of palladium but indifferently with nickel, which was also inferior in the several solvents.

The technique of high pressure catalysis has received intensive study at the Fixed Nitrogen Research Laboratory and two papers on this subject by Ernst [32] are of interest. Kileffer [33] has described a high pressure catalyst testing equipment installed by L'Azote, Inc. and Larson and Richardson [34] have discussed the preparation of fused oxides as starting materials for the preparation of ammonia making catalysts. Evans and Newton [35] have supplied some useful experimental data for catalysts in the production of hydrogen from steam and water gas, concerning which, hitherto, only the data in patent specifications were available. This group of papers is of importance in the new industrial high pressure synthesis of methanol, the thermodynamics of which has been discussed by Kelley.[36]

[30] J. Am. Chem. Soc., **47**: 3051; 1925.
[31] J. Am. Chem. Soc., **48**: 778; 1926.
[32] Ind. Eng. Chem., **17**: 775; 1925. **18**: 664; 1926.
[33] Ind. Eng. Chem., **17**: 789; 1925.
[34] Ind. Eng. Chem., **17**: 971; 1925.
[35] Ind. Eng. Chem., **18**: 513; 1926.
[36] Ind. Eng. Chem., **18**: 78; 1926.

Chapter XXXII.

Explosives.*

By Charles E. Munroe,

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There is a broad and there is a limited meaning to the term "explosive," for it is properly used in designating any solid or liquid or gaseous compound or mixture of substances which can be exploded through the influence of any initiating cause, but technically it is applied to such substances as are especially manufactured and sold for use in firearms, and other military devices, and in blasting, or to substances having similar characteristics. Those explosives which occur in nature or are formed casually in mining and industrial operations or are formed intentionally in the cylinders of internal combustion engines are of equal scientific interest with and of quite as much economic importance as the explosives manufactured for sale.

Research is being actively conducted with all categories of explosives, but probably to a greater extent with explosive mixtures of combustible gases, vapors, or dusts, with air or other supporters of combustion, than with manufactured explosives. Thus the investigations of the British Safety in Mines Research Board under the leadership of R. V. Wheeler has resulted in many valuable publications, of which Paper No. 18, "The pressure wave sent out by an explosive," by Payman and Robinson; No. 20, "The electric ignition of firedamp: alternating and continuous currents compared," by Wheeler; No. 24, "The ignition of firedamp by momentary flames," by Walls, Wheeler, Rintoul and White, and No. 27, "Firedamp explosions: the projection of flame," by M. J. Burgess, have appeared during the past year.

Through a coöperative arrangement between the above-mentioned Board and the U. S. Bureau of Mines for the study of

* Comprising in part the report of the Committee on Explosives Investigations for the year 1925-1926. Charles E. Munroe, Chairman; O. M. Hustvedt and C. G. Storm.

explosions in coal mines, there has already resulted "Extinction of methane-air flames by some chlorinated hydrocarbons," by H. F. Coward and G. W. Jones,[1] and "Extinction of methane-air flames by helium," by the same authors,[2] while the "Extinction of methane flame by diluent gases" has resulted from the independent studies of H. F. Coward and F. J. Hartwell.[3] In the course of the investigations being carried on in this field at the University of Michigan, G. G. Brown[4] has sought to resolve some confusion that existed by his article on "Gaseous explosions. II. Homogeneous and heterogeneous reactions defined and classified," while F. W. Stevens[5] at the Bureau of Standards has sought, through the data obtained from his soap-bubble bomb experiments to develop mathematical expressions for "The rate of flame propagation in gaseous explosive reactions." Of special interest and importance are the reports of Bone and his associates[6] on "Gaseous combustion at high pressures" and on the "Combustion of well-dried carbon monoxide and oxygen mixtures,"[7] leading to the conclusion that the presence of steam is not always essential to the ignition and explosion of $2CO + O_2$. It is recognized that these and other recent investigations of phenomena occurring within matter in the gas phase lead to but further developments in the field cultivated by Bunsen, Berthelot, Mallard and Le Chatelier, Michelson, Dixon, Bone, Mixter and many other earlier investigators, and that because of the more easily controlled conditions, the simplicity of the systems employed, and the greater ease and accuracy with which observations and measurements may be made upon them, information regarding the initiation, propagation and dissemination of explosions and detonations, which apply to all explosives systems, could not have been so readily, and perhaps not at all, for some features, obtained from the study of explosives in the liquid and solid phases. Likewise, the investigations of Midgeley and his associates on vapor phase systems, and particularly on the suppression of detonation in such systems, have been of general benefit.

The explosive phenomena occurring in coal-dust-air and coal-dust-gas-air mixtures and in other combustible mine dusts mixtures is a constant subject of study by the U. S. Bureau of Mines

[1] Ind. Eng. Chem., 18: 970; 1926.
[2] Bur. Mines Repts., Investigation No. 2757.
[3] J. Chem. Soc., 1926: 1522.
[4] Ind. Eng. Chem., 17: 1229; 1925.
[5] J. Am. Chem. Soc., 48: 1896; 1926.
[6] Proc. Roy. Soc., 110, A, 645; 1926.
[7] Proc. Roy. Soc., 110, A, 615; 1926.

in its laboratories, its experimental mine and in mines in commercial operation, and by similar organizations in the principal coal mining countries of the world. During the past year some 20 progress reports and reviews have been made at conferences held at the Pittsburgh Experiment Station of the U. S. Bureau of Mines covering many phases of gas and dust explosions, the physical and chemical characteristics of "explosives" and the manometry of explosions. At one of these conferences J. W. Paul dealt with "Unsolved problems in mine explosions," pointing out that as eye-witnesses were usually killed, the findings in the case were almost wholly dependent on circumstantial evidence, and he then related from a wide experience in such examinations certain phenomena and appearances that were sought in coal mine explosions, and especially depositions of coke and soot as regards their locations with relation to the direction of propagation of the explosion waves and their conditions of formation. And he asks, "What is the physical action controlling the deposit of the coke, and how may this be linked up with the direction of travel of the explosion?" Soot, in the form of slender strings, is often found near a closed end of an entry adhering to the roof and other surfaces. It contains from 8 to 15% of ash. "Is this material evidence of the presence of gas at the time of the explosion?" The surface of the coal near closed ends or tight places often shows evidence of flakes of coal having spalled off as though a flame had lingered at this place. It presents every indication of a torch having been applied to it. "Is this due to a sudden reduction of surface pressure or to heat?" In some long mine entries or haulage roads evidence of exceptional violence has been observed. Apparently, a detonation had taken place. "What are the conditions favorable for such detonation, assuming that there are obstructions to furnish turbulence?" In some large mines where the explosion has traveled throughout the mine and where there were many closed ends there was evidence of secondary explosions. "With a dust explosion is it possible to build up suddenly sufficient pressure to create sufficient heat to inflame a cloud of dry coal dust?" A recognized factor in promoting the formation of explosive dust mixtures is found in the fineness of the dust, since this increases the exposed surfaces of the combustible and permits of its more ready admixture with and suspension in the gaseous component. An important contribution to the study

of this condition is "Determination of the fineness of coal dust," by E. F. Craig.[8]

The devising of means for the suppression or restricting of the explosion of dust mixtures in mines is also under active investigation, attention now being focussed on stone dust, which acts as an incombustible diluent of the explosive mixture. Results of the cooperative agreement set forth above are embodied in "Stone dust as a preventive of coal-dust explosions. Comparative tests," by G. S. Rice and R. V. Wheeler.[9] In this are found the data of tests of English coal dust tested at Bruceton, Pa., and of American coal-dust tested at Eskmeals, England.

In my address [10] to the American Chemical Society in 1909 I pointed out the hazards of combustible dusts in many industries following the capacity of such dusts to form explosive mixtures with the air about them. For several years past these industrial dusts, the circumstances under which they form explosive mixtures, the methods by which such mixtures become ignited, and the means for the prevention of such explosions or the mitigating of their effects have been the subject of investigation by D. J. Price and his associates of the Bureau of Chemistry, U. S. Department of Agriculture. Numerous publications have resulted from these investigations. The varieties of industries subject to this menace have been greatly extended, the initiating causes found to be more numerous and the conditions more varied than had previously been recognized. Friction and the accumulation of static charges being recognized as frequently acting initiators of dust-air explosions, means were devised for their elimination. In his paper on "Dust explosions in industrial plants," H. B. Brown [11] advocates the reduction of the oxygen content of air in the grinding machines by the introduction of inert gases such as N or CO_2. For many substances a reduction of the O content to 12% is sufficient, but for sulfur dust this reduction must be carried to 8.5%.

Manufactured or commercial explosives may be classified in many ways. (1) From their constitutions: into explosive compounds, such as nitroglycerin, and explosive mixtures, such as dynamite; (2) From their behaviors toward one another: into initiators, such as mercuric fulminate, and responders, such as

[8] Safety in Mines Research Bd. Paper No. 25; 1926.
[9] Safety in Mines Research Bd. Paper No. 13; 1925.
[10] J. Am. Chem. Soc., 31: 317; 1909.
[11] Ind. Eng. Chem., 17: 902; 1925.

picric acid; (3) From their behaviors in exploding: into low explosives, such as gunpowder, and high explosives, such as guncotton; (4) From their uses: into propellents, such as smokeless powder, and blasting agents, such as TNT; (5) From their capacities to meet certain specified requirements for particular uses as, for instance, in coal mines when they fall into the classes of "permitted" or "permissible" explosives if they meet the tests or non-permitted or non-permissible if they have not.

The quantities of explosives produced are quite considerable even in time of peace. Thus, in the United States there was manufactured in 1925, taking explosives of all kinds, 551,188,384 pounds. In the banner year for industrial explosives, 1923, the amount returned was 577,246,570 pounds. Naturally during the war this amount was greatly exceeded, but this was abnormal. Black blasting powder, which was the dominant industrial explosive through five centuries, is passing. The peak of its production in the United States was reached in 1907 when 287,000,000 pounds were manufactured. In 1925 only 160,940,900 pounds were produced; a falling off of 40%.

The fate of blasting powder was spelled by dynamite of which, originally, the dominant component was nitroglycerin. With the invention of coated ammonium nitrate by Penniman for an explosive component of the dope ammonia dynamites assumed importance and they now constitute the larger part of the many permissibles. With the development of the nitroglycerin-nitrocellulose colloids by Nobel, the gelatin dynamites came into vogue and are today meeting with increased use in metal mining. In the meantime di- and poly-nitroglycerins were introduced as components because they prevented the products containing them from freezing at the natural temperatures to which they were exposed in practice, thus eliminating the recurrence of the many disastrous accidents which attended the thawing of frozen dynamite.

During the war there arising a shortage of glycerin, sugars, both sucrose and glucose were mixed with the glycerin and nitrated, but the results were not altogether satisfactory. Much consideration was also given to various glycol nitrates. Unexpectedly, since the war, the shortage of glycerin has persisted because of its increasing use in other industries and in antifreeze liquids for automobiles and, because the present sources of supply cannot be greatly increased, this has fostered the development of

substitutes. Within the past year the value of ethylene glycol dinitrate has been so demonstrated that it is being introduced into dynamites in part substitution of the nitroglycerin. Its properties as an explosive component range near to those of nitroglycerin and it imparts L.F. properties to the composition. As ethylene is obtained from alcohol, by-product coke oven gas, illuminating gas, natural gas and other sources, the likelihood of a shortage with an enhanced cost for dynamite is now remote.

It has been recognized that the behavior of an explosive and the uses to which it may be properly put depend in large measure on the form of the reactions it undergoes on explosion and the character of the products formed. That is, its suitability for a given use is largely determined by the composition of its products, the rate at which they are evolved and the temperature they acquire. Also, from a precise knowledge of the quantity and kind of products we may calculate other characteristic data. The investigation of the products from black gunpowder was undertaken by Bunsen and Schischkoff, Noble and Abel, and Debus notably. Subsequently, high explosives were so studied by Sarrau and Vieille, Poppenberg and Stephan, Kast, Munroe and Howell, Robertson and Garner, Audibert and others. From the nature of the apparatus employed a low loading density and small charges of explosives were necessitated. In "An apparatus for studying gases of explosives detonated under confinement," J. E. Crawshaw and G. W. Jones [12] describe an apparatus of their devising through which they generate and recover the detonation products under conditions closely approaching those attending the actual use of such explosives in mining. Charges of 150 grams, or larger, may be detonated in this apparatus and the products collected as discharged, under pressure, in air or nitrogen. Already several publications have resulted from the tests with this apparatus.

In one of the earliest publications from the Bureau of Mines Munroe and Hall pointed out the menace to miners from the noxious, or poisonous, gases evolved from explosives. The kind and quantity of these vary with the composition of the explosive, the nature and proportion of the cartridge wrapper, the degree of confinement of the charge, and the character of the reaction it undergoes. That is, the gaseous products vary according as to whether the explosive is (1) burned unconfined, (2) burned confined, (3) weakly detonated by a low grade detonator, or (4)

[12] Eng. Mining J.-Press, 120: 965-7; 1925.

completely detonated by a high grade detonator. Numerous instances of poisoning from CO and N-oxides evolved from explosives burning unconfined or from blown-out shots might be cited. The most devastating were those occurring on the U. S. S. *Trenton* and *Mississippi*. These have led to an extensive review of the subject by D. C. Walton [13] published under the title "Gas poisoning following powder explosions," prior to experimental investigations of the behavior of smokeless powder subsequently undertaken at the Edgewood Arsenal. There are now two great incentives to thoroughness in loading boreholes and to the use of high grade detonators in the charges. The first is to secure the highest efficiency from the charge of explosive used. The second is to avoid the payment of indemnity under the Compensatory Acts now in vogue, for it is becoming increasingly common to claim injury from "powder fumes."

In his "Experimental researches on the explosive and the shock waves" P. Laffitte [14] by photographic observations finds that, after the explosion or detonation wave has passed completely throughout the length of the "file" of the high explosive, there is a shock wave projected from the far end of the file and that this shock wave has initially a higher velocity than the detonation wave within the file. Laffitte observed the propagation of the shock wave in combustible and incombustible gases and through solids. It proceeds for a notable distance beyond the end of the file but its rate falls off very rapidly. There is now much activity in photographic observations on explosives phenomena and the technique is being rapidly improved.

A. E. Malinowski [15] observed the phenomenon of "Ionization in the wave of propagation of explosions" by passing mixtures of air with hydrogen or hydrocarbons through an iron tube and measuring the pressures and extent of ionization when the explosion wave proceeded normally and when it was made to pass through a strong electric field. The explosion proper was preceded by an initial wave in which ionization occurred, the degree of ionization being reduced when the wave passed through the electric field owing to the latter removing ions or electrons. Upon using a mixture of air and benzene vapor the explosion was completely stopped when the initial wave passed between plates charged to a potential difference of 110 volts. The degree of

[13] U. S. Naval Medical Bull., **22**: 259; 1925.
[14] Ann. Phys., **4**: 587; 1925.
[15] J. chim. phys., **21**: 469; 1924.

ionization was greater when the velocity of the explosion wave was increasing than when its velocity was decreasing. A greater part of the ions carried forward by the explosion wave recombine and the author holds that the energy thus set free maintains the explosion, but the small residue of ions carried forward by the explosion wave from one layer to the next tends to accelerate the reaction. It is these ions that are removed by the electric field.

With the development of commercial methods for the liquefaction of air and the isolation of liquid oxygen, attention was focused on the finding of uses to which these new commercial products could be put. One of the earliest suggested uses of liquid oxygen was in the compounding of liquid oxygen explosives, styled, for convenience, "LOX." A multitude of mixtures of carbonaceous and metallic combustible matters with liquid oxygen have been experimented with and some of them used in practice. Perhaps the most extended and detailed account of its use, together with costs including that of liquefying the oxygen, is found in "Liquid oxygen explosives at Pachuca" by M. Kuryla and G. H. Clevenger.[16] LOX found its opportunity during the war as an emergency explosive, for, unlike black blasting powder, dynamite and other commercial explosives in general use, it can be produced without drawing on the supplies of niter, nitric and sulfuric acids and other materials required in the production of military explosives. The story of its use was told by G. S. Rice[17] in his "Development of liquid oxygen explosives during the war," from which it appears that Germans used LOX extensively in non-gaseous coal mines, in quarrying and in iron mines as well as for demolition purposes in French steel plants. LOX has several proven advantageous characteristics. Because of the volatility of the liquid oxygen component the life of the explosive is brief. Because of this the explosive must be fired promptly after the explosive is made and loaded into the borehole. As a consequence, LOX is quite unsuited to use in uprisings or in committing outrages, nor does it offer a temptation to thieves, all of which are important considerations in unstable communities in the midst of which important mines are not infrequently operated. With a liquefaction plant installed the manufacture of LOX is a relatively simple matter and the mine has a constantly dependable supply. Moreover, it is relatively cheap. Kuryla and Clevenger

[16] Trans. Am. Inst. Mining Met. Eng., Preprint No. 1210-M.
[17] Bureau of Mines, Tech. Paper No. 243.

report, from their experience, that the total cost of LOX, equivalent in breaking effect to 40% gelatin dynamite, was 9.19 to 9.50 cents per pound. This may prove a matter of first importance in a remote region. Although, under normal conditions, LOX does not appear able to compete successfully with commercial explosives, yet its value as an emergency explosive justifies endeavors to secure and place on record the fullest and most detailed information concerning it and, therefore, it is a continued subject of research. Moreover, the products of the liquefaction of air may find other uses about a mine. They may be used in refrigeration. The oxygen may be used in compound blowpipes in the repair or construction of machinery or in smelting. Obviously, a mine equipped to produce liquid oxygen is better able to arrange terms for purchase of explosives than one without such an equipment.

G. St. J. Perrott,[18] in his "Properties of liquid oxygen explosives," has determined experimentally the explosive strength of lampblack cartridges, of definite dimensions and in which the lampblack had been packed to a fixed density, for definite intervals of time after removal from the liquid oxygen by which they were saturated, and he found the available life of these cartridges before formation of CO in the products of explosion began was 10 minutes, while their explosive life was 20 minutes. The explosive strength, he finds, is at a maximum when the cartridge is removed from the dipping container, and decreases slowly and fairly regularly for 20 minutes, after which the strength falls off rapidly. If a higher packing density is used the cartridge after the first minute contains insufficient oxygen for complete combustion to CO_2, yet it may be fired after 10 minutes' evaporation with 15% greater strength than the lighter packed cartridge, and after 25 minutes it develops as great strength as the lighter cartridge. These data indicate that, where the presence of CO is not detrimental, greater explosive effect may be obtained by increasing the packing density. The particle size of the absorbent was found the most important factor in determining the rate of evaporation. The excess oxygen adherent to the cartridge as first removed from the dipping container was found to contribute to the efficiency of the explosion products because of the low heat of vaporization of liquid oxygen. LOX should be fired by detonators. It can be exploded by fire or fuse, but the result is uncertain.

[18] Trans. Am. Inst. Mining Met. Eng., Preprint No. 1388-A.

LOX cartridges burn without detonation. When confined in a bore hole lampblack and gas-black filled cartridges, on ignition, sometimes burn without exploding, but very frequently they detonate. Cartridges containing hydrocarbons, such as petroleum oil, gilsonite or carbene, always detonate if ignited under confinement. There is reason to believe that, when such charges are fired by ignition only, their rate of detonation is considerably less than when they are fired by detonators and, therefore, the brisant effect from such charges is below their capacity. However, since in many instances a propulsive effect only is desired, investigations are in progress for ascertaining the feasibility of blasting with certain mixtures without detonation.

One naturally queries if LOX may have any other military importance than as a supplementary explosive to relieve the drain on the raw materials demanded for military explosives. It is recognized that military authorities are by necessity relieved from the observance of those proper regulations which govern the handling, transportation and storage of industrial explosives. The statement of a single one of the many exceptions makes this obvious. The taking of industrial explosives into the homes, which miners are prone to do, is unqualifiedly condemned as an unwarranted hazard which has been a frequent source of utterly inexcusable accidents, yet it is a prime requirement that a warship, carrying hundreds of officers and men, shall also carry in close proximity to the quarters of these persons large stores of high explosives and propellents. In war the ammunition dumps of the Army must be in close proximity to the guns to be served. The quantities of explosives to be stored awaiting the emergency of war are far in excess of any industrial needs, but responsible officers and other personnel must live in close association with these great stores to inspect and protect them.

May it not be possible that the war-heads of automobile torpedoes and depth bombs may be charged with LOX manufactured on board the vessels from which they are discharged, thus reducing the quantity of explosives to be carried on board or to be stored at arsenals or depots through long periods of time and at great expense and hazard.

The means by which such a result may be attained is by no means an obvious one, for it must be ascertained if a liquefaction plant of the required capacity could be installed and operated on board ship; if the disadvantages resulting from the rapid boiling

off of the oxygen could be overcome, or, even perhaps, utilized in the propulsion of the torpedo or bomb; and if the method of saturating the charge could be so controlled that the residual charge at the time it is to be fired is at or near its maximum efficiency. The liquefaction of air, moreover, is not free from hazards, as pointed out by Ernest Fyleman [19] and Georges Claude.[20]

On September 21, 1921, there occurred at Oppau, Germany, one of the most devastating explosion catastrophes ever known. As is generally known, it was found that an explosion had taken place in a mass of stored fertilizer consisting of a mixture of NH_4NO_3 and $(NH_4)_2SO_4$, presumably composed of two molecules of the former to one of the latter. That any explosion whatever, and especially that an explosion of the intensity and magnitude which was manifested, could occur in a composition such as this seemed incredible and this problem has ever since occupied the attention of many investigators in Germany, England and this country. In November, 1925, H. Kast [21] began the publication, in monthly instalments, of the results of the investigations in Germany. The story is not yet completed and the cause, if found, is not yet indicated, but already the singular fact is experimentally demonstrated that the rate of detonation of a mixture of ammonium nitrate (a known explosive substance) with ammonium sulfate (heretofore regarded as an inert, inexplosive substance) is greater than the rate of detonation of ammonium nitrate *per se*, and that also the sensitiveness of ammonium nitrate is increased by admixture with ammonium sulfate or other substances.

Although ammonium nitrate has often been the subject of study as recorded in "The explosibility of ammonium nitrate," by Charles E. Munroe,[22] it was a surprise to learn that when in transportation barrels of it, which had been in storage at Muscle Shoals for some years, took fire, probably owing to the friction of the nitrate impregnated staves on one another.[23]

Another explosion accident which has led to a special research was that which occurred at Harvard University on May 19, 1922, while oxygen was being compressed into a cylinder. The investigations were conducted by M. D. Hersey and his associates at

[19] J. Soc. Chem. Ind., 42:152; 1923.
[20] Compt. rend., 182: 356-8; 1926.
[21] Separates with Z. ges. Schiess Sprengstoffw. from 20, No. 11 to date.
[22] Chem. Met. Eng., 26: 535-42; 1921.
[23] Ind. Eng. Chem., 17: 819; 1925.

the Bureau of Mines Experiment Station, Pittsburgh. The results of their investigations were résuméd in an address on "Oxygen-oil explosions" to the Technical Staff at Pittsburgh, at one of the conferences referred to above, by Professor Hersey and it is amazing how small an amount of oil or other combustible material, such as a minute fragment of coal, suffices to produce an ignition in compressed oxygen. Investigations were made under pressures up to 3600 pounds to the square inch and it was found that spontaneous ignition, that is, ignition produced without the application of flame or spark, began to occur at pressures of 500 pounds per square inch. This was particularly the case if the compression was suddenly developed as, for instance, in the filling of an empty cylinder from one charged at high pressure. It was pointed out that it was well-nigh impossible to "crack" a valve. Indeed one was surprised at the suddenness with which a valve "opened," thus releasing a high pressure promptly. The differences found for the ignition temperatures of oils and other lubricants at atmospheric pressure and pressures above 500 pounds per square inch in oxygen were surprising. One would hardly expect that the ignition temperature of glycerin would fall from 412° C. at normal to 205° C. (a reduction of 207°) at high pressure, or that it would be found that, although the average temperature for the explosibility of oil in compressed air is decidedly higher than in oxygen, nevertheless the minimum temperatures in air are substantially the same as the average temperatures in oxygen. In other words, the margin of safety between air and oxygen is decidedly less than most of us supposed before this investigation was undertaken. Another important observation was that of the behavior of metals, the ignition temperature of iron falling some 330° C. when the oxygen pressure reached 2000 pounds per square inch. Under such circumstances, iron-turnings spontaneously ignited. This tends to explain the heating not infrequently noted in charging oxygen cylinders. Copper and brass appeared to burn but slightly, usually melting. These results suggest that brass and copper are probably much safer materials to use for manifold construction and other apparatus for use with compressed oxygen than iron or steel, for should any condition cause the manifold or piping to become heated to the melting point, it would probably simply release the oxygen without taking fire.

The consideration of statements submitted above cannot fail

to suggest many topics for further research. A practical topic of much importance is the determination of the cause of the reduction in sensitiveness to detonation of the gelatin dynamites in storage. The X-ray study of explosive substances is likely to reveal much interesting information of their molecular structures and possibly the position of strains within them. The reaction of explosive substances to free cathode rays or electrons from a semi-permeable Coolidge tube would prove likely to give interesting results. Possibly the much desired smokeless igniter for smokeless powder charges might result, unless the reaction initiated took the form of detonation. These are a few of many suggestions which may be made in this field.

Chapter XXXIII.

Water and Sewage.

By Edward Bartow,

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The report of the Advisory Committee on Official Water Standards,[1] published in April, 1925, has influenced the work during the year in a significant manner. It is a revision and extension of the first report published in 1914, which set standards for the quality of drinking water supplied to the public by common carriers in interstate commerce, and not only improved the quality of water furnished on the common carriers but also led to improvement of water furnished in public water supplies. The second report strengthens the bacteriological standards, adds statements concerning the source and protection of water supplies, and sets standards for physical and chemical characteristics.

In line with the report of the Committee on Standard Methods of the U. S. Public Health Service, there have been studies in the differentiation of the colon-aërogenes group in drinking water. J. J. Hinman, Jr.,[2] considers a differentiation to be of value. The coli section of the group is the most significant in forming a judgment and warrants a more adverse report. Butcher[3] has suggested the use of chinic acid in the differentiations within the colon-aërogenes group. H. G. Dunham, M. H. McCrady, and H. E. Jordan[4] have suggested briliant green bile as worthy of more attention.

Because of the higher standard of the U. S. Public Health Service water officials throughout the country are being more and more careful of the condition of their water. Chlorination is in

[1] U. S. Treas., Dept. Pub. Health, Rept. **40**: 693; 1925.
[2] Am. J. Pub. Health, **15**: 614; 1925.
[3] J. Am. Water Works Assoc., **15**: 171; 1926.
[4] J. Am. Water Works Assoc., **14**: 535; 1925.

general use and secondary chlorination has been proposed by W. W. Brush [5] for the New York water supply at the reservoir at Hillview. Secondary chlorination will overcome secondary pollution in open reservoirs or below surface conduits.

Accepting the idea that iodine deficiency is the cause of goiter, several studies have been made of the relation between iodine deficiency and goiter. In Michigan, E. D. Rich [6] has shown the relation between goiter and iodine in the water supplies and claims that the best method is addition of iodine to table salt. H. W. Clark,[7] after making studies in Massachusetts, has come to the same conclusion that iodized salt is the best method of overcoming iodine deficiency, and that addition to water is wasteful. However, J. A. Goodfellow [8] reports the continuous addition of sodium iodide to water at Ilkeston and Heanor, whereas at Rochester, New York, the iodide is applied intermittently. At Minneapolis, Minnesota, it is recommended by A. F. Mellen [9] that 10 parts per billion of sodium iodide be added to the municipal supply. The cost he estimates would be 1½¢ per capita per annum. A study of the distribution of goiter and iodine in water supplies by J. C. Hathaway [10] has shown that they are in inverse ratio. Evidence so far would indicate the value of the use of iodine and further experiments on a large scale will undoubtedly be made.

Studies made throughout a number of years by the U. S. Public Health Service on the pollution and natural purification of the Ohio River were made public during the year 1924-5 by W. H. Frost and H. W. Streeter.[11] They found that the total nitrogen, organic and oxidized nitrogen vary within too slight a range to afford precise measurement of stream pollution. Oxygen consumed values are less sensitive. Bacteria increase for a time below sewers and then decrease. The Pittsburgh and Wheeling districts do not cause as great an increase as would be expected, possibly due to inhibitory action of acid mine wastes.

Four papers by Frost, Theriault, Streeter, and Hoskins [12] present an admirable summary of the notable investigations carried on by the U. S. Public Health Service. The papers tell of the

[5] J. Am. Water Works Assoc., **14**: 526; 1925.
[6] J. Am. Water Works Assoc., **14**: 325; 1925.
[7] Eng. News-Record, **95**: 470; 1925.
[8] Munic. County Eng., **75**: 526; 1925.
[9] Eng. News-Record, **95**: 352; 1925.
[10] Proc. Soc. Exptl. Biol. Med., **22**: 183; 1924.
[11] U. S. Pub. Health Service, Bull. 143; 1926.
[12] Proc. Am. Soc. Civil Eng., **51**: 1809-1855; 1925.

scientific studies of the rate of deoxygenation of polluted waters, the rate of atmospheric re-aëration of sewage polluted streams, and give quantitative studies of bacterial pollution and natural purification in Ohio and Illinois rivers. Studies in the pollution of bodies of salt water have been carried on under the auspices of the Metropolitan Sewage Commission of New York and are reported by Kenneth Allen.[13] As the results of years of study, standards of cleanness have been fixed for the harbor.

Wastes from many cities contain the effluent from gas works. Phenol is a common constituent and its determination indicates the extent of gas works pollution. L. R. Vorce[14] reports a method for the determination of small quantities. Calcium and magnesium are first removed, then hydrogen peroxide, free from benzene compounds is added, the mixture allowed to stand over night, then concentrated to 200 c.c., acidified with citric acid, and distilled. The phenol is determined colorimetrically by the Folin and Denis reagent.

The railroads were pioneers in softening water for their boilers. An account of what is done in providing a railroad's water supply is given by R. C. Bardwell.[15] Increasing attention is given to water softening, and transportation cost is reduced.

There has been some difference of opinion concerning the value of zeolite-treated water for boilers. S. T. Powell and J. H. Wolfe[16] tell of zeolite-treated water in use at Baltimore. They declare there is no corrosion and no scale formation, but that foaming is somewhat increased.

S. W. Parr and F. G. Straub[17] report that embrittlement of boiler plate is caused by the combined action of stress and chemical attack. The stresses are inherent in the construction and in the operation of the boiler, while the chemical attack is caused by sodium hydroxide in the boiler water. The presence of sodium sulfate in the feed water and undecomposed sodium carbonate in the boiler water tends to retard the embrittling effect of carbonate waters, and if these chemicals are present in proper proportions, they will stop it entirely.

One of the causes of corrosion in boiler water is oxygen. W. J. Rigley, Jr.,[18] describes tests which he has made. Oxygen

[13] Proc. Am. Soc. Civil Eng., 52: 520; 1926.
[14] Ind. Eng. Chem., 17: 751; 1925.
[15] Railway Age, 79: 517, 885; 1925.
[16] Ind. Eng. Chem., 17: 584; 1925.
[17] Univ. of Illinois, Eng. Expt. Sta., Bull. 155: 1-60; 1926.
[18] Chem. Met. Eng., 33: 163; 1926.

can be removed by boiling at 140° F. under the required reduced pressure. Oxygen can also be removed by rusting with iron.

Municipalities are beginning to follow the railways in water softening procedure. Many cities throughout the country are softening water with lime, several new installations having been put in during the past year. C. S. Timanus [19] states that Springfield, Illinois, has planned a water softening and filtration scheme. It was placed in operation in June or July, 1926. Lime is used to soften, a Dorr clarifier to remove sludge continuously, carbon dioxide to recarbonate. A similar plant has been operated a few years in Oklahoma City. Newark, Ohio, has started a water softening plant described by C. T. Kaiser.[20] Softening by lime, continuous sludge removal, a carbonation with scrubbed boiler gases, are similar to those at Springfield and Oklahoma City. The continuous sludge removal, which is being put in also in the large new plant at Kansas City, seems to be an improvement over the old settling basins and will probably be adopted in all new installations.

Sodium aluminate has been put on the market on a commercial scale and its use in water treatment is increasing. Experience with it has been described by J. P. Brownstead, E. T. Edwards, E. E. Smith, and C. P. Hoover.[21] Its use during experimental periods gave as a rule good results. Hoover estimated it cost from 74-135% more than an equivalent mixture of sodium carbonate, lime, and alum.

On the Rock Island Railroad P. M. LaBach [22] states that the addition of sodium aluminate to sodium carbonate and lime allows the use of less material and gives softer water. If the material has special advantages, the cost may be reduced and it may be more generally adopted.

Dry feed of chemicals is being used more and more. C. E. Rhyme [23] states that dry feed methods are better than wet feed, cleaner, labor saving, time saving, and less troublesome.

The large sewage disposal works at Milwaukee [24] and Indianapolis have been put in operation. These are the largest activated sludge plants in the world. The one in Milwaukee has a capacity

[19] J. Am. Water Works Assoc., **13**: 630; 1925.
[20] Eng. News-Record, **95**: 174; 1925.
[21] Ohio Conf. on Water Purification, 4th Ann. Rept. for 1924: 31; 1925.
[22] Am. Railway Eng. Assoc., Bull. **27**: 277; 1925.
[23] J. Am. Water Works Assoc., **14**: 36; 1925.
[24] Eng. Contr., **65**: 115; 1926. Eng. News-Record, **95**: 75; 1925.

of 85,000,000 gallons daily and was put in operation June 26, 1925. The Indianapolis plant [25] started operating in June, 1925.

In addition to the large plants at Milwaukee and Indianapolis, large plants are being constructed by the Sanitary District of Chicago. Other plants are being put in operation or being constructed and further studies on the activated sludge process have been made. F. W. Harris [26] has made a study of the use of filter beds and activated sludge. He concludes that the activated sludge requires the smallest area and that on the whole for aëration in the activated sludge process, diffusion is better than mechanical agitation. Activated sludge experiments on packing house wastes have been carried on at Houston, Texas, by G. L. Fugate.[27] A plant consisting of a grease collector, Dorr clarifier, Simplex surface aëration, effluent oxidation tank, and final clarifier will be used. The sludge will be conditioned with SO_2 and mixed with tankage and pressed hydraulically. The dried sludge contains a minimum of 7% nitrogen and 3% H_3PO_4.

According to R. V. Orbison [28] the activated sludge plant at Alhambra, Calif., has been in operation for more than a year. The effluent is good and is used for irrigation. The sludge is dried on Oliver filters and spread on farm land with a manure spreader.

K. Imhoff [29] recommends the disposal of excess activated sludge by digestion. Activated sludge 0.5 part, fresh sewage sludge 0.5 part, and digested sludge 1 part is the best mixture. 16 liters per capita per day of gas is produced. The amount of digested sludge is increased and the amount of activated sludge decreased.

B. Nerreter [30] describes the use of gas from Imhoff tanks in city mains. Gas from two tanks is mixed with city coal gas supply. An analysis of the gas shows CH_4 80%, CO_2 17.4%, O_2 0.2%, N 2.4%, heating values 7653 kg. cal. cu. m.

Sierp [31] also tells of recovery of gas in sewage disposal. Tanks are covered so gas can be collected. Three cubic meters per year per individual are collected, analyzing: CH_4, 75-85%, CO_2, 15-20%, N_2O 5%. F. L. Campbell and William Rudolfs [32] found no hydrogen and but little hydrogen sulfide in the tanks examined.

[25] Eng. News-Record, **95**: 180; 1925.
[26] Contract. Record, **39**: 926; 1925.
[27] Eng. News-Record, **94**: 443; 1925.
[28] Eng. News-Record, **95**: 714; 1925.
[29] Eng. News-Record, **94**: 936; 1925.
[30] Gas Wasserfach, **69**: 185; 1926.
[31] Gas Wasserfach, **68**: 773; 1925.
[32] Eng. News-Record, **95**: 552; 1925.

For treatment of packing house sewage, W. C. Moor and W. P. Wayne [33] have used screens and clarifiers which remove 74% of the suspended matter. The effluent to the city sewer increases the load so the city treatment plant at Fort Worth, Texas, cannot handle it.

A review of work done during the year shows problems that may be profitably studied. These include:

1. The significance of B. aërogenes when present in drinking waters and its differentiation from the colon section of the colon-aërogenes group.
2. Double chlorination of drinking water has been practiced in several places. It may be adopted more generally if conditions warrant, especially in large plants or where there is trouble in obtaining a sterile supply.
3. If the relation of iodine deficiency and goiter has been established, we need to know the best, most economical, and most effective methods of adding the iodine.
4. U. S. Public Health Service will undoubtedly continue its study of river pollution and natural purification. There are more problems connected with various streams throughout the country.
5. The delicate test for phenol suggests the possibility of more delicate tests for other trade wastes, especially those from the organic chemical industries.
6. Most of our railroads are using softened water. Many cities and manufacturing establishments have an opportunity to decrease losses and increase the efficiency of their plants in this way.
7. The applications of base exchange minerals in water softening and treatment.
8. The causes of embrittlement have been explained by the combined action of stresses and chemical attack. What are the limits of various ingredients allowable in the water in the boiler?
9. Sodium aluminate is a new water treatment chemical whose use is hardly known.
10. Methods of dewatering and drying activated sludge are not yet entirely satisfactory.
11. Activated sludge may be digested in Imhoff tanks and the gas obtained therefrom used as a source of heat and power.

[33] Ind. Eng. Chem., 18: 239; 1926.

Chapter XXXIV.

Coöperative Research Between Industries and Universities.

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Actual coöperation in research between the universities and industries of this country has involved a great array of suggestions and plans, some of which have worked well while others have met with decided failure. In general, we may classify this active coöperation under three heads: Retainerships, Fellowships and Scholarships.

That policy wherein a member of a university faculty is paid a retainer, or consultation fee, and is called upon for advice and assistance to the regular research personnel of an industry, is of course ideal from the standpoint of both the university and the industry. This policy is steadily gaining in favor and gives promise of becoming the goal toward which our university men may direct their outside activities; the prerequisite, however, that the university man shall possess outstanding ability and be able to sense the practical significance of investigational steps, restricts considerably this policy and confines the selection of such men to the upper division of our professorial group. The lower division of this professorial group—made up of instructors and teaching assistants—requires yet a few years' training and study. That practice where members of a university faculty are employed during the summer months in outside work falls also under this particular classification.

The establishment of fellowships at universities under the direction of competent authorities offers another favorable plan for promoting research and maintaining promising young men in the proper atmosphere for study. This policy is steadily growing

and contributing much both in the solution of many problems and in the building up of a larger and larger research clientele. Young men launched in this career where practically their entire time is given over to research should constitute excellent material from which our future university research professors can be selected. The position of research professor is altogether too rare in America. The complex problems before us today require the highest type of investigators. The university stands preëminent in affording the broadest scope for study in arts and sciences untrammeled by mundane restrictions. It therefore behooves universities to establish research professorships on their staffs at every opportunity.

The establishment of scholarships, as our third class, is very widely distributed throughout the country. These scholarships are largely based upon stipends of not much in excess of $750 a year and are largely held by undergraduates or graduates who are more or less occupied with regular college duties. Such scholarships, as founded at the universities by individuals or organizations, should be construed to a large extent as gratuities for needy and praiseworthy students and no attempt made on the part of the donors to secure therefrom scientific data of publishable value. At those universities where fellowships have been set up by industries it would appear most appropriate that scholarships of lesser stipend might likewise be offered in order to stimulate advanced students and prepare certain promising candidates for the highly prized and more lucrative fellowships.

It will be seen from the above that the most direct method of building up a greater and greater coöperative spirit between the universities and the industries will proceed from that type of coöperation which we have just described as a fellowship. As a matter of general interest, we may cite here the general scheme for classification of fellowships, as drawn up by the Central Petroleum Committee of the National Research Council in its distribution of funds and direction of research under the auspices of the American Petroleum Institute:

Research Associate—Stipend not below $3000.
Research Fellow—Stipend $3000 and downwards, not to include $2000.
Junior Research Fellow—Stipend not in excess of $2200.
Research Assistant—Stipend $600 up to $1200.

The salaries attached to the representatives of any one class may overlap somewhat the other classes but the general idea remains

intact and we have a classification not inconsistent with professorial ranks. The research associate is the counterpart of the college professor. Several of the universities at which we have established these research associates have already given the rank of associate professor to the incumbent of this class and, furthermore, no university work is attached to the position. The research fellows are being appointed to assistant professorships and the research assistants to assistantships at our universities. There is no obligation on the part of the universities to accept these rulings of the Central Petroleum Committee, but, nevertheless, there has been an open-hearted and wholesome concurrence in favor of all possible means of giving proper recognition to these research appointments. We look upon the system as one of the most promising yet proposed between universities and industries. The results of the researches are to be published, and wherever discoveries should be secured by patent these patents are to be taken out and made available for the benefit of the public.

When now we consider the fellowships carrying lesser stipends we come upon the great bulk of grants established by industries in our several universities. The fellowship holders are expected to spend all or nearly all of their time upon the problems at hand and in the course of a year or more the results of their work find expression through scientific journals. In the ever increasing number of industrial fellowships established at our universities we see the greatest hope for coöperative research. Young men will rejoice in the opportunity offered for several additional years of research under the guidance of erudite men and will reap therefrom worlds of benefit from an educational point of view, no matter whether immediate results may or may not be forthcoming.

The industries are intent upon maintaining a higher and higher degree of efficiency and they are thoroughly cognizant of the rôle which research must play in this program. It is not to be expected that all industries will establish fellowships providing for the entire livelihood of young men at our colleges and universities. Many will await the results of appointments already made and especially will they follow closely this admirable plan on the part of Mr. John D. Rockefeller of the Standard Oil Company and Mr. H. J. Halle, President of the Universal Oil Company, in their establishment of the $500,000 research program to cover the next five years of research on fundamental problems of

petroleum under the auspices of the American Petroleum Institute as has just been discussed.

In the meantime, the Division of Chemistry and Chemical Technology has undertaken to encourage every sort of coöperation possible between the industries and the universities. To this end problems of industrial importance have been secured by the Division and, through its Chairman, these problems have been given out to young university men wherever a particular research interest could be aroused. To some it may seem odd that our Division is emphasizing this particular mission when it is known that we are primarily committed to the establishment of fellowships.

From some quarters, indeed, we are well aware that university men look askance at this new venture, seemingly because they have been wont to await the establishment of a fellowship before instituting the research. The explanation is certainly simple enough. Industrial leaders know at least 300 university chemists of distinction and entertain no compunction whatsoever in placing fellowships under these men for the prosecution of researches. There are, however, many more problems for research than it is possible for these same distinguished chemists to undertake, even though they were each to be assigned one hundrd fellowships.

Of the many colleges and universities in this country, possibly 500 may be considered as having facilities of some sort for some type of scientific study, but outside of possibly 150 academic centers for chemical research the great majority of chemists in academic positions have little or no entrée to industrial plants and are far out of touch with the immediate trends necessary for industrial growth.

During the past fifty years we have witnessed a slow but steady development in American industries. Indeed, the strides made in the past five years actually surpass those of any preceding decade. The problems of our industries have become the problems of greatest moment. Our preservation and future prowess are bound up in the solution of these problems. It is the call to research and upon research alone our future as a nation must stand.

The problems that we have taken from the industries are to a large extent of industrial bent. It so happens that the greater number fall in the domain of organic chemistry; yet this is not surprising when we recognize that practically 75% of all chemical researches in America involve organic compounds. These prob-

lems, furthermore, may be considered as of seemingly less importance, yet, nevertheless, they serve admirably the purpose. For, whether the investigation savours either of fundamental or applied research, sooner or later the student comes upon the fundamental concepts that lie beneath and to some phase of this revelation he is ready to devote his energies. Thus, our aim remains primarily the introduction of the study of fundamental problems. It should be borne in mind that industrial laboratories are far better equipped for the applied researches than the university laboratories can ever hope to be.

In the main we have approached more particularly the instructors and assistant professors of those universities and colleges somewhat removed from active chemical manufacturing centers. The spirit of enthusiasm that pervades this younger class is a decided asset in an attack upon more or less resistive problems.

When once a problem is taken up by a university man a report from time to time on the progress of work is made to the Division. When, from these reports, the Chairman of the Division is convinced that the investigator is making progress of such a nature and to such an extent that the particular industry concerned with the problem may be keenly interested in the research, then these reports are referred to this industry.

If the industry through its research department evinces no interest in the report, then the problem drops out or, as is usually the case, it is presented to some other industry; but if no interest can be solicited from any industry then the problem no longer claims our attention. It will be observed that we have here no expenditure of time or money on the part of the industry, save the supplying of various special chemicals sometimes needed for the research, and hence the industry stands to lose nothing. On the part of the university man the only possible loss is the time devoted to the undertaking, but this time is not supposed to cover a period of more than a month or six weeks, the work being done during one or two afternoons a week. This time could hardly be construed as an entire loss to any one really and whole-heartedly intent upon finding a problem for research. It is of course a gamble on the part of the university man as far as time is concerned, but every research worker knows that real problems involve a bit of prospecting.

When, on the other hand, the particular industry concerned shows an interest in the reports from the investigator, as sub-

mitted by the Division, and is desirous that the investigator proceed with the work he has begun, then it becomes the duty of the industry to pay a regular stipend directly to the investigator. This stipend is rated on the actual time per week given to the research and varies considerably among the industries.

In other words, in this plan we have virtually the genesis of a fellowship. Unrestricted publication is permitted the investigator. If a patent is to be taken out the particular industry must be given at least a shop right therein; the final status, however, rests upon the financial arrangements between the contracting parties. In many instances where the investigator proves his ability, we shall now have every reason to expect that the industry having learned of his ability in this particular direction will more than likely embrace the opportunity of establishing a fellowship at the university where the investigator is resident. Naturally, the industry could not be expected to establish fellowships without some knowledge concerning the investigators, and thus we find a way of guiding the industries to men of creative minds. In the early stages of the work, before any progress has been noted, it is not necessary that the name of the investigator be made known to the industry nor the name of the industry to the investigator.

In this new plan of cooperative research we have a number of distinct purposes in view:

1. Bringing the immediate problems of the day to the attention of the chemists throughout the country:—*Disseminating research.*

2. Supplying many chemists out of contact with distant industries with just those problems particularly suited to their own fancies:—*Fitting the problem to the man.*

3. Developing the knowledge and competency of the young college scientist; a thing which the college is so prone to repress by burdening him with work more adequately and better accomplished by the average stenographer:—*Utilizing fertile minds for mental labor.*

4. Preparing the way for more highly developed and experienced chemists in the future employ of the industries and the universities:—*Improving and broadening the chemical situation.*

5. Making it possible for an industry to foster a large number of embryonic researches without actually increasing its regular research staff:—*Establishing university connections for an industry.*

6. Opening the doors of the industries to suggestions from men

of versatile minds and thus inspiring their own research staffs with new ideas:—*Revivifying industrial research men.*

7. Introducing a scheme whereby any individual, whether he be connected with an industry or not, can have recourse to research men willing to tackle whatever problem may arise when promise of financial return is not out of range:—*Centralizing university laboratories for research suggestions.*

When the research men of the universities and industries are thus brought into closer relationship, a great array of possibilities is bound to arise at every turn. Opportunity for summer work will be open to the university men at many of the industrial laboratories and later regular retainerships will accrue to the university men who have made their way.

The system as outlined above is already set into operation and results promise well for the enterprise. We realize, however, that no plan is perfect and that possibly there are many who may agree with some of the critics who pronounce the plan too much of a subsidy and a gamble.

Now, the subsidizing of young men to engage in fundamental research—if such the plan is construed—is just what we have intended to accomplish:—anything in fact to get the brilliant young men out of the doldrums of a listless existence. Indeed, after several years spent in the university many of the young men grasp the first opportunity and betake themselves to industrial laboratories. Here, however, the efforts of research are so sharply focused in closely circumscribed fields that free play of imagination ofttimes succumbs. What science needs is the conservation of this particular class of men of keen imagination and constructive ability in a locale primarily suited to free and independent thinking. They should be permitted to run rampant as it were and to vary their activities as their moods prescribe.

As the years go by, these same young men, through retainerships and consultation fees, may well be earning salaries that will enable them to remain in those highly honored academic positions in which the highest interest of science and the university is served. We are all subsidized by some organization and the plan offered is merely one that young men may be subsidized by organizations of high financial standing.

In the criticism that the university man takes all the chances and that the odds are against him, we have again exactly the conditions we desire. The industries are not asking for the work.

They are overwhelmed today with problems of their own making. Why should they fire into the air when no game is in sight? The problems that they give us carry much of future potential value and when workers are found who can make any headway in these studies then the industries are the first to sense the possibilities of carrying the results to their logical conclusions. The university man can have no influence upon the direction of industrial activities, but, if he hits upon some lead then he may enter immediately into deliberations with industrial scientists and will have earned for himself the highest respect and confidence—a position that must redound to the good name of the university he represents.

Those who would have the industries hand out fellowships on a silver platter to whomsoever cometh have little or no knowledge of the enormous expense incurred by our industrial research laboratories. The annual outlay of money for researches of various character in any one of our large industrial organizations would pay the annual running expenses of any one of our large universities. Is it possible for a young instructor to be given a fellowship by one of these universities merely for the asking, or even after years of research work? Yet here the industry practically promises the equivalent of a fellowship on a few weeks' notice if the young man can demonstrate his ability to handle the problem. If this is gambling, then we pray that we may have more and more gambling.

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